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ENVIRONMENTALLY-INDUCED PASSIVITY

OF ALUMINUM ALLOYS AND ALUMINUM METAL

MATRIX COMPOSITES

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Arlington, VA 22217-5000
Attn: Dr. A. John Sedriks

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This final report presents a summary of the work performed under Contract No. N00014-88-K-0034. One of the goals of the research carried out was to develop corrosion protection methods for Al-based materials which can replace the presently used chromate conversion coatings with modified surface layers of equal or even better resistance to localized corrosion. The past work first evaluated the use of rare earth metal chlorides (REMC) for the passivation of Al alloys and Al/SiC by a simple immersion treatment. Very corrosion resistant surfaces have been obtained in this manner which did not show any localized corrosion during exposure to aerated NaCl for periods up to 60 days. In an attempt to shorten the passivation time, a passivation treatment in solutions of $CeCl_3$ and $Ce(NO_3)_3$ has been developed. Very corrosion resistant surfaces have been produced in a process in which immersion in $CeCl_3$ and $Ce(NO_3)_3$ was followed by an electrochemical treatment in Na_2MoO_4. Modified surfaces produced in this process do not support oxidation or reduction processes to any significant extent which explains the observed excellent corrosion resistance. Pitting of Al 6061 was not observed during exposure to NaCl for 60 days.

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ABSTRACT

This final report presents a summary of the work performed under Contract No. N00014-88-K-0034. One of the goals of the research carried out was to develop corrosion protection methods for Al-based materials which can replace the presently used chromate conversion coatings with modified surface layers of equal or even better resistance to localized corrosion. The past work first evaluated the use of rare earth metal chlorides (REMC) for the passivation of Al alloys and Al/SiC by a simple immersion treatment. Very corrosion resistant surfaces have been obtained in this manner which did not show any localized corrosion during exposure to aerated NaCl for periods up to 60 days. In an attempt to shorten the passivation time, a passivation treatment in solutions of $CeCl_3$ and $Ce(NO_3)_3$ has been developed. Very corrosion resistant surfaces have been produced in a process in which immersion in $CeCl_3$ and $Ce(NO_3)_3$ was followed by an electrochemical treatment in Na_2MoO_4. Modified surfaces produced in this process do not support oxidation or reduction processes to any significant extent which explains the observed excellent corrosion resistance. Pitting of Al 6061 was not observed during exposure to NaCl for 60 days.

TABLE OF CONTENTS

1.0 INTRODUCTION

Due to the toxic nature of chromate ions, one of the most common and successful methods of corrosion protection of Al alloys will not be available anymore in the near future. Among the advantages of chromate conversion coatings are their ease of application, their commercial availability, the fact that they are self-healing and their high electric conductivity. Considering these very desirable properties, it is not difficult to understand that it will not be easy to find a replacement for chromate conversion coatings which provides similar degrees of corrosion protection while maintaining all other advantages of the present coating systems.

Under the contract funded by ONR (Contract No. N00014-88-K-0034), various approaches have been used to develop a chromate-free conversion coating for Al alloys and Al-based metal matrix composites (MMC) and/or to produce a "stainless" aluminum by various methods of surface modification. The approach used was based on earlier work (1) in which a number of methods of corrosion protection were evaluated for use with Al alloys and Al-based MMCs. These methods included chromate conversion coatings, anodizing, the application of polymer coatings and chemical passivation in $CeCl_3$ (2-7). For the latter process, very corrosion resistant surfaces were obtained by simple immersion in $CeCl_3$ for 7 days. For Al 6061 which had been passivated in $CeCl_3$ localized corrosion in the form of pitting or crevice corrosion did not occur during immersion in 0.5 N NaCl (open to air) for over 90 days (1-7) which is a very significant achievement considering the susceptibility of untreated Al alloys to pitting in chloride media. Similar results were obtained for Al 7075-T6, but not for the -T73 condition, where Cu precipitates caused corrosion due to the establishment of the Al/Cu couple. For the Al/SiC MMC, pitting was not observed for more than 81 days, however crevice corrosion was observed for this material after about one week. Since this problem did not occur for any of the Al alloys or the Al/graphite MMC, which was covered with an Al 6061 face sheet, it was attributed to the presence of the SiC particulates.

Since the initial evaluation of the chemical passivation process had provided very encouraging results for improved corrosion protection of Al alloys and Al-based MMCs, a more detailed study has been carried out in the present project. The mechanism of chemical passivation has been studied in more detail for rare earth metal chlorides (REMC) such as $LaCl_3$, $NdCl_3$ and YCl_3 using a combination of electrochemical and surface analytical techniques applied to passivated pure Al, Al 2024, Al 6061, and Al/SiC. Based on the results obtained with anodic and cathodic polarization curves, it has been concluded that chemical passivation reduces both the passive current density and the rate of the reduction of oxygen. However, the pitting potential remained the same for both untreated and passivated surfaces exposed to aerated NaCl.

While immersion of Al-based materials in solutions of REMCs can produce very corrosion resistant surfaces, the required immersion time of 4 to 7 days provides problems for practical applications. Modifications of this procedure were therefore evaluated which include immersion in $Ce(NO_3)_3$ at elevated temperature for several hours followed by immersion in $CeCl_3$ at elevated temperature for several hours. The resulting surface films provide the same degree of corrosion protection as those obtained previously by immersion in $CeCl_3$ for 7 days at room temperature. However, the total time for passivation was only about 4 hours. It was observed that the initial surface properties of the

as-received Al-based materials played an important role in the efficiency of the passivation process. Therefore, a deoxidizing step was used in some cases which removed the oxide layer on the as-received surface. The deoxidized surface was then baked in an oven at elevated humidity levels to produce a new air-formed oxide layer. Chemical passivation of this type of surface has usually been very successful for pure Al and Al 6061. For Al/SiC the corrosion resistance became less with increasing SiC concentration. An important result of this study was the observation that pit growth rates could be determined from impedance spectra recorded at the open-circuit potential (8). So far, it has been necessary in the few published papers dealing with this problem (9, 10) to apply a potential which is more positive than E_{pit} in order to obtain pit growth rates. The approach developed under this contract based on electrochemical impedance spectroscopy (EIS) is considered to be a major advance in the study of localized corrosion which -- from a practical point of view -- is one of the most important forms of corrosion, but has not benefited enough from the recent advances in theoretical and experimental techniques.

Molybdate has been used for a long time as corrosion inhibitor. Recently, the research group at Martin Marietta has evaluated methods of corrosion protection of Al which included production of alloys by RF magnetron sputter deposition onto single crystal Si wafers (11) in a project which has also been funded by ONR. The corrosion resistance of the resulting surface alloy layers was evaluated by salt spray tests and by potentiodynamic polarization curves in which the pitting potential E_{pit} was determined. E_{pit} was found to increase from about -700 mV vs SCE for the untreated surface to -100 mV for surface concentrations of Mo between 5 and 10 at.% (11). Shaw et al. (12) reported results obtained with an electrochemical process in which Mo claimed to be in the +4 and +6 state was incorporated into the passive film. This anodic polarization procedure resulted in an increase of E_{pit} by about +500 mV. The authors concluded from this shift of E_{pit} that the modified passive film was significantly more resistant to pitting than the untreated surface. However, it has to be kept in mind that the resistance of Al alloys to pitting cannot be judged by the value of E_{pit} alone (13). In fact a repeat of the procedure described by Shaw et al. (12) in this laboratory has shown that upon immersion into 0.5 N NaCl pitting occurred for such samples after a short time in the same manner as for the untreated surfaces. A new procedure has therefore been developed at CEEL which combines the $CeCl_3/Ce(NO_3)_3$ treatment discussed above with an anodic Mo treatment. The resulting surface layers have very interesting and unusual properties which include excellent corrosion resistance. The results obtained with this new procedure and with the other techniques discussed above are described in detail in this report.

2.0 RESULTS AND DISCUSSION

The main effort in the past three years has been devoted to the evaluation of the chemical passivation process which consists of immersion in rare earth metal (REMC) chlorides. While this process has been very successful for REMCs such as $CeCl_3$, $NdCl_3$ and $PrCl_3$, it requires long passivation times of several days to one week. Various modifications of the process were therefore evaluated which reduced the passivation time to less than one day. One of these modifications was the incorporation of molybdate in the modified film by an electrochemical treatment. Finally, surface modification by an applied ac potential was evaluated for Al 2024 for which the other treatments did not give very satisfactory results.

2.1 Experimental Procedures

For as-received samples, the surfaces were first degreased using Alconox detergent, rinsed with distilled water to remove the detergent and dried by air. The samples were immersed in hot hexanes at 66°C for 15 minutes, rinsed with distilled water and dried by air. The third step was then to clean the surfaces in an ultrasonic cleaner in acetone at 30°C for 10 minutes, rinse with distilled water and dry with air. Finally, the Alconox detergent was used to remove residual organic reagents. The samples were then rinsed with distilled water to remove the detergent, dried with air and put into a desiccator.

For polished samples, the surfaces were polished with 600 SiC paper. After polishing, the cleaning procedure was the same as for the as-received samples.

For samples with the deoxidizing treatment, the surfaces were cleaned following the procedures as described for as-received samples. After the alkaline cleaning step, the surfaces were deoxidized in a chromate-HNO_3 bath (Deoxidizer 17, Amchem) or in a H_2SO_4-HNO_3-H_2SiF_6 bath (Aluminum Deoxidizer, Diversey Wyandotte 560) for 10 minutes at room temperature.

In order to produce a uniform oxide film before the passivation treatment, the polished or deoxidized samples were baked in an oven at 100°C for at least 24 hours.

2.1.1 Passivation Procedures

For Al 6061, the passivation solutions included 5 mM $CeCl_3$, $NdCl_3$, $PrCl_3$, YCl_3, $LaCl_3$, $CeCl_3$+$NaNO_3$, 10 mM $CeCl_3$, $LaCl_3$, $NdCl_3$, or $PrCl_3$. The exposure lengths for passivation were 7, 15 or 30 days. The passivation temperature was 22°C$\pm$1°C. For pure Al, Al 2024 and Al 6061/SiC, the passivation solution was 5 mM $CeCl_3$ for 7 days. EIS data were obtained at certain times during passivation.

2.1.2 Corrosion Tests

Samples with or without chemical passivation were exposed in 0.5 N NaCl (open to air) at room temperature. The corrosion behavior during exposure to NaCl was monitored using EIS. In some cases, weight loss data were also obtained. The surfaces of representative samples were evaluated with SEM/EDAX and/or AES.

2.1.3   Electrochemical Impedance Spectroscopy (EIS)

The EIS measurements were carried out at the corrosion potential E_{corr} with a Solartron model 1250 Frequency Response Analyzer (FRA) and a Solartron model 1286 potentiostat.   A saturated calomel electrode (SCE) which was coupled capacitively to a Pt wire to reduce the phase shift at high frequencies (14) was used as the reference electrode.   The EIS data were analyzed with the software packages COATFIT and PITFIT which have been developed in this laboratory.

2.1.4   Cyclic Polarization Curves

These measurements were carried out using a PAR 173 potentiostat with a 276 GPIB interface card which was controlled by an Apple IIe computer. Cyclic polarization curves were measured during chemical passivation and during exposure to 0.5 N NaCl. A scan was usually started at the corrosion potential E_{corr} in the anodic direction. It was reversed when a vertex current density of 100 $\mu A/cm^2$ was reached.

2.1.5   AC Passivation

For Al alloy 2024, passivation was carried out in 5 mM $CeCl_3$ with an applied square wave voltage of -640 mV $\pm$ 120 mV vs SCE for three days. After this time, a square wave voltage with a $\pm$ 20 mV amplitude was continuously applied for three days.

2.1.6   Scanning Electron Microscopy (SEM) and Auger Electron Spectroscopy (AES)

SEM analysis was used to observe the surfaces before and after chemical passivation and after exposure to 0.5 N NaCl. Energy dispersive X-ray analysis (EDAX) was applied to determine the chemical element distribution on the surface. AES was used to determine the composition of the passive films and to provide concentration profiles of the elements in the modified surface layers.

2.2 Experimental Results and Discussion

2.2.1   Chemical Passivation in Rare Earth Metal Chlorides (REMC)

2.2.1.1   EIS-Data

For pure Al which had been passivated for 7 days in 5 mM $CeCl_3$ the impedance spectra remained capacitive in the entire frequency range during immersion in 0.5 N NaCl for 14 days (Fig. 1).   The polarization resistance R_p which is inversely proportional to the corrosion rate exceeded 10^6 ohm.cm^2 and the interfacial capacitance C_{dl} was about 27 $\mu F/cm^2$.

For degreased Al 2024 R_p decreased during passivation in 5 mM $CeCl_3$ and the capacitance increased with increasing passivation time. Pitting occurred after immersion in NaCl within one day. Similar results were obtained for a sample which had been polished before passivation. The use of the ac passivation process in 5 mM $CeCl_3$ produced much better results and pitting did not occur for 35 days in NaCl. Fig. 2 shows typical impedance spectra after 1, 10 and 35 days immersion. R_p decreased from 8.4×10^6 ohm.cm^2 after 1 day to 0.5×10^6 ohm.cm^2 after 35 days. In the same time C_{dl} increased from 11.2 to 16.5 $\mu F/cm^2$ which could be
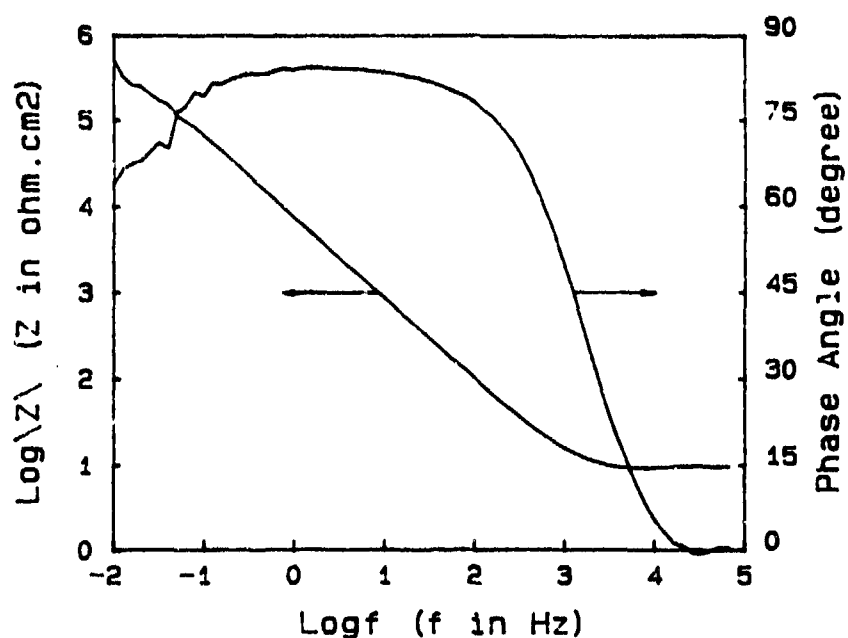
Fig. 1   Bode-plots for as-received Al after passivation in 5mM CeCl$_3$ for 7 days and immersion in 0.5 N NaCl for 14 days, A = 20 cm^2.
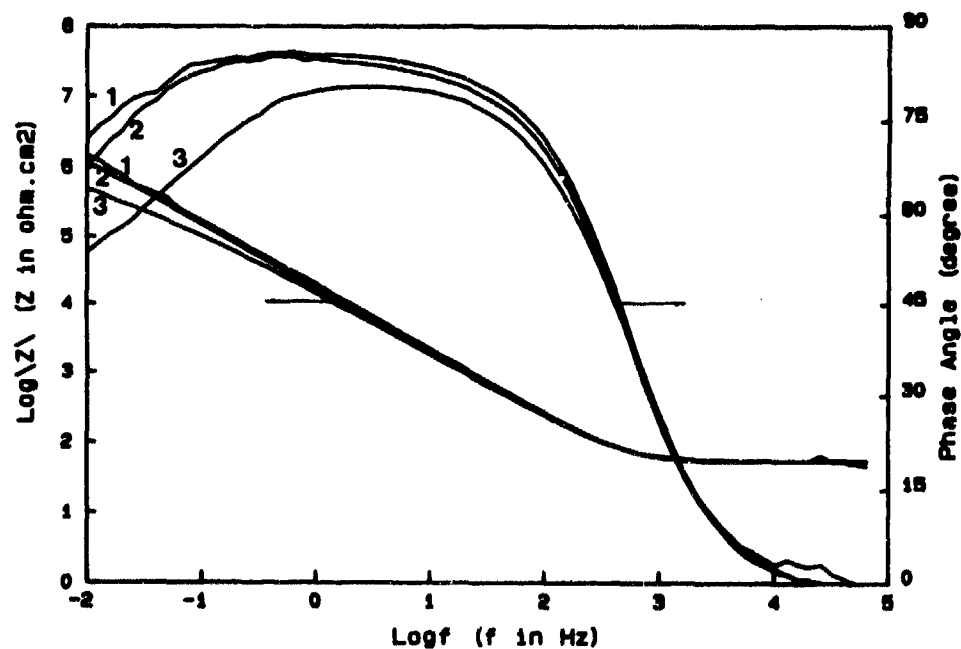

Fig. 2   Bode-plots for Al 2024 after AC passivation in 5mM CeCl$_3$ for 6 days and immersion in 0.5 N NaCl for one day (curve 1), 10 days (curve 2) and 35 days (curve 3), A = 20 cm^2.

due to thinning of the film and/or an increase of its dielectric constant.

For Al 6061-T6 the passivation time was varied from 7 to 30 days and the concentration of the REMCs was varied from 4 to 30 mM. Fig. 3 shows impedance spectra in 5 mM $CeCl_3$ for Al 6061 which was degreased only before passivation. The capacitive nature of the spectra and the high R_p values show that the modified surface is very corrosion resistant. Similar results have been obtained for passivation in 5 mM $LaCl_3$, $NdCl_3$ and $PrCl_3$ (Fig. 4) (16).

The impedance spectra for Al 6061 which had been degreased and passivated in 5 mM $CeCl_3$ for 7 days are shown in Fig. 5 as a function of immersion time in NaCl, while in Fig. 6 both the $CeCl_3$ concentration and total exposure time to NaCl have been varied. Similar spectra have been obtained for passivation in $NdCl_3$ (Fig. 7) and $PrCl_3$ (Fig. 8). Very good corrosion resistance is indicated by the capacitive nature of the impedance spectra and the high values of R_p. On the other hand, passivation in 5 mM $LaCl_3$ or YCl_3 did not produce surfaces with high resistance to localized corrosion as indicated by the different frequency dependence in the low-frequency region in Fig. 9 which is in agreement with the pitting model described elsewhere (3-8). The impedance spectra for these two cases did not differ very much from that for untreated Al 6061 which is also shown in Fig. 9 (curve 3). For all three tests pitting and uniform corrosion were observed visually.

The impedance data for Al 6061 (degreased) have been summarized in Table 1 for passivation in $CeCl_3$, $LaCl_3$, $NdCl_3$, $PrCl_3$, $CeCl_3$ + $NaNO_3$ and subsequent immersion in 0.5 N NaCl (open to air). For comparison, data are also listed for the untreated sample. In Table 1, t_{pass}, $R_{p(pass)}$ and $C_{p(pass)}$ are the passivation time, polarization resistance and capacitance obtained at the end of the passivation process, while t_{corr}, $R_{p(corr)}$ and $C_{p(corr)}$ are the corresponding values for the corrosion process in NaCl which in most cases lasted for 60 days. In general, an increase of the concentration of the REMCs adversely affected the corrosion resistance of the modified surface which might be due to the increased chloride ion concentration in the passivation solution.

Similarly, increased passivation times were not beneficial (Table 1). For passivation in $CeCl_3$ $R_{p(corr)}$ exceeded 10^6 ohm.cm^2 except for a concentration of 10 mM and 7 days passivation and for 30 mM concentration and 7 or 15 days passivation. For $LaCl_3$ only passivation at 4 mM for 7 days produced acceptable $R_{p(corr)}$- values. For passivation in 10 mM $NdCl_3$ $R_{p(corr)}$ was equal or exceeded 10^6 ohm.cm^2 for all three passivation times. However, satisfactory results were not obtained for a $NdCl_3$ concentration of 25 mM. For passivation in $PrCl_3$ very good results were obtained except for passivation times of 30 days. Excellent results were also achieved when a mixture of 5 mM $CeCl_3$ and 5 mM $NaNO_3$ was used. For the untreated samples $R_{p(corr)}$ was very low (Table 1) and localized corrosion was observed after only a few days. The results obtained for passivation in YCl_3 are not listed in Table 1. As shown in Fig. 9, curve 2 pitting was indicated after only a few days exposure to NaCl. No clear correlations of $C_{p(pass)}$ or $C_{p(corr)}$ with the quality of the modified surface films can be made at present. However in a number of cases shown in Table 1, larger values of C_p coincide with the less corrosion resistant surfaces.

The surface properties and corrosion resistance of the modified Al 6061 surfaces which have been prepared by chemical passivation can be compared with those obtained by treatment in commercial chromate conversion coating solutions. Fig.
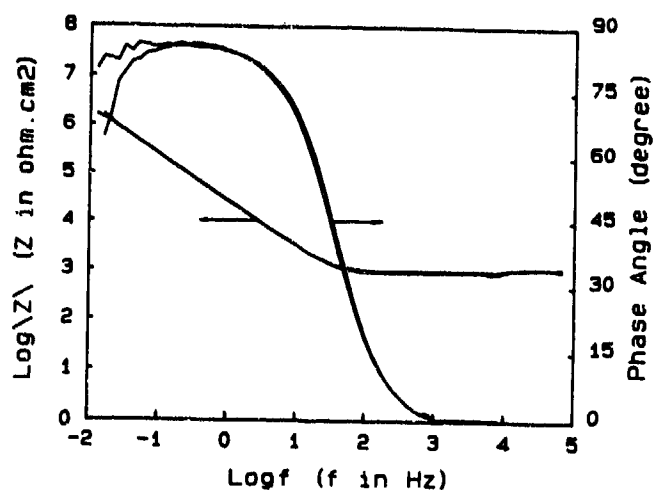
Fig. 3   Bode-plots for Al 6061-T6 (degreased) during passivation in 5mM $CeCl_3$ for one day (curve 1) and 7 days (curve 2), A = 20 cm^2.
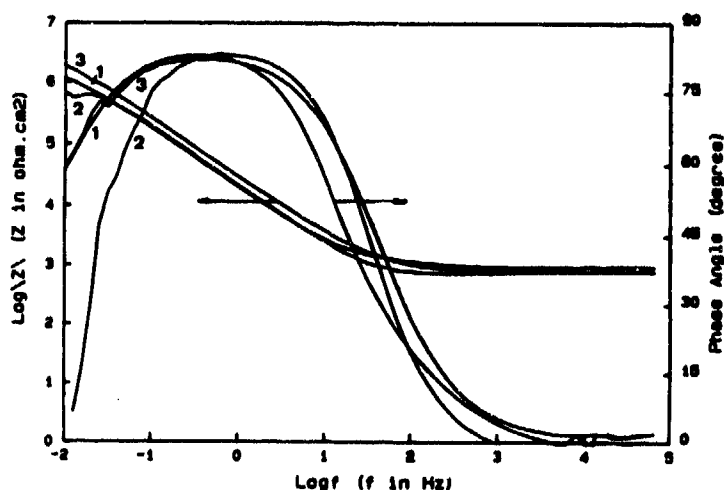

Fig. 4   Bode-plots Al 6061 (degreased) during passivation in 10mM $PrCl_3$ (curve 1), $NdCl_3$ (curve 2), and $LaCl_3$ (curve 3), A = 20 cm^2.
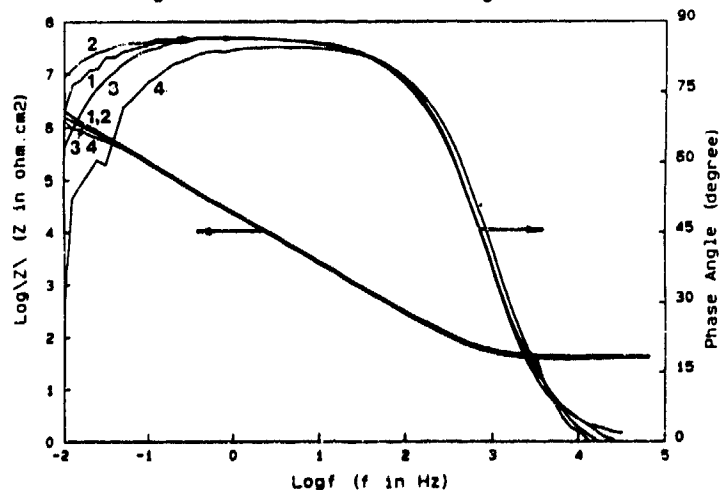

Fig. 5   Bode-plots for degreased Al 6061 in 0.5 N NaCl after passivation in 5mM $CeCl_3$ for 7 days, A = 20 cm^2. Curve 1 = one day; Curve 2 - 7 days; Curve 3 - 32 days; Curve 4 - 60 days.
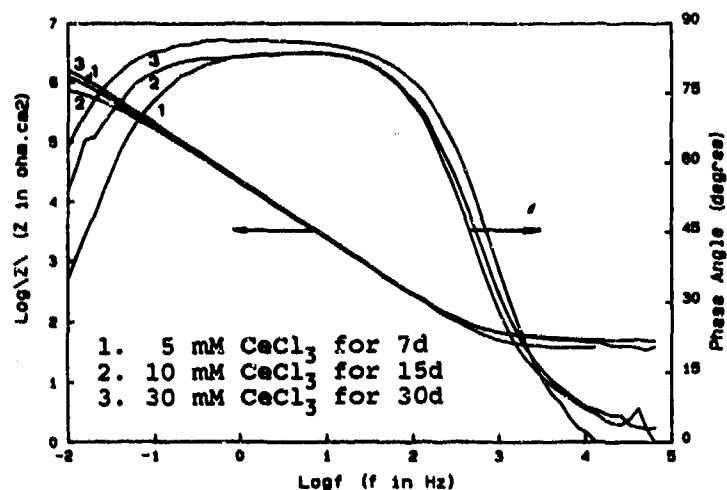
Fig. 6   Bode-plots for $CeCl_3$ treated Al 6061 exposed
         to 0.5 N NaCl for 60 days, A = 20 cm^2.
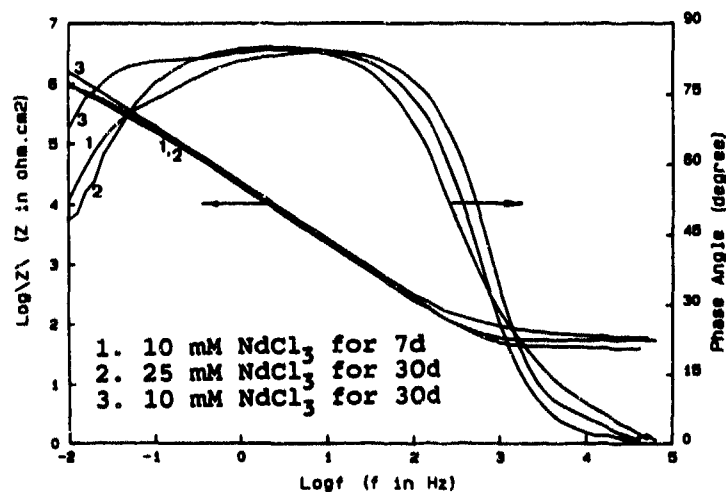

Fig. 7   Bode-plots for $NdCl_3$ treated Al 6061 exposed to 0.5 N NaCl
         for 60 days.
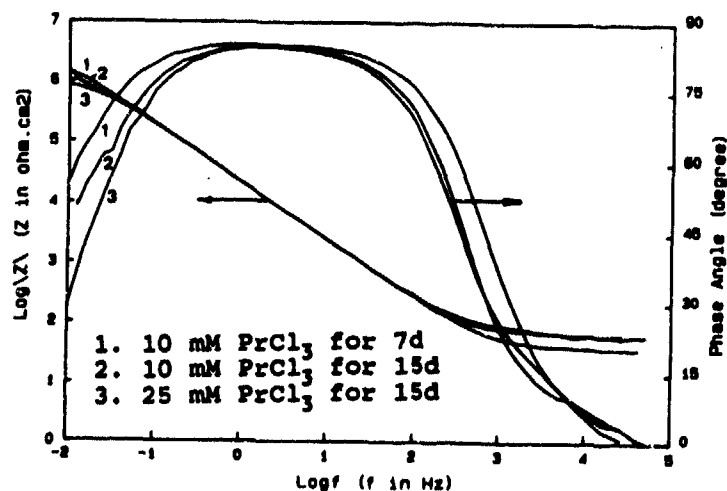
Fig. 8   Bode-plots for $PrCl_3$ treated Al 6061 exposed to 0.5 N NaCl
         for 60 days.

Fig. 9   Bode-plots for LaCl₃ and YCl₃ treated Al 6061 during exposure to 0.5 N NaCl.
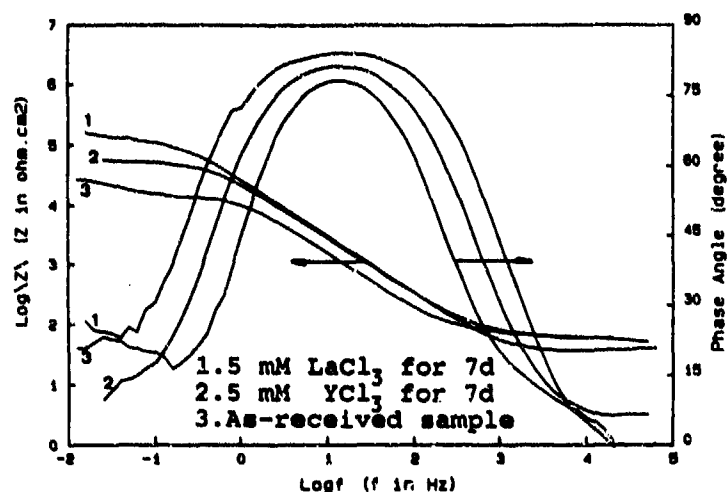
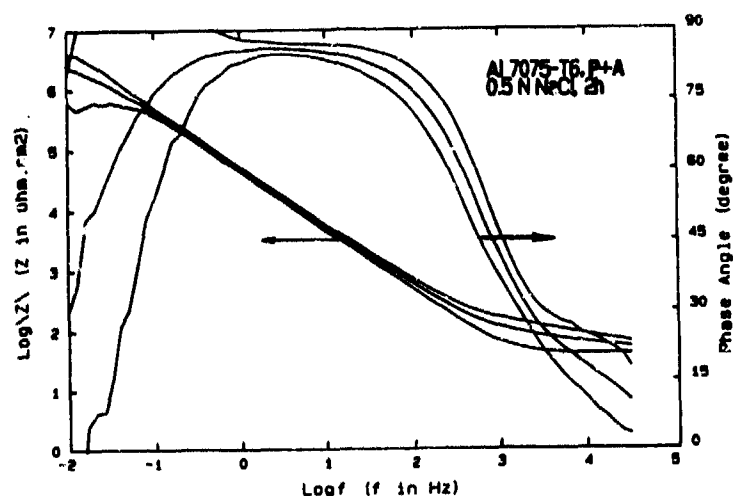Fig. 9   Bode-plots for $LaCl_3$ and YCl_3 treated Al 6061 during exposure to 0.5 N NaCl.

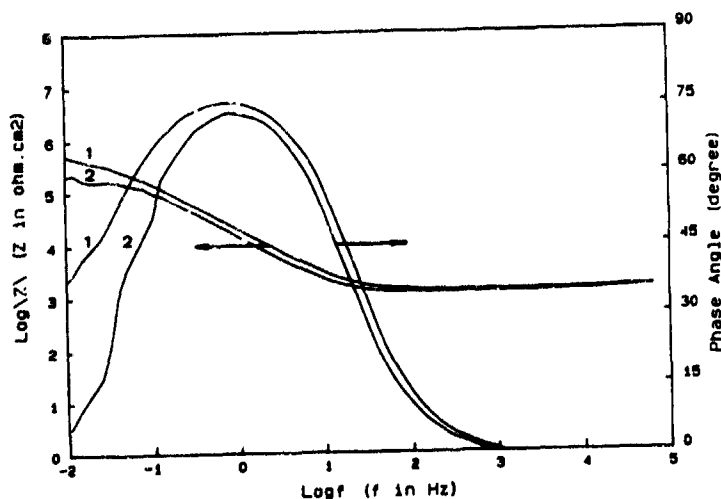Fig. 10   Scatter bands for conversion coated Al 7075-T6 (Parker+Amchem, Alodine 600); 2h exposure to 0.5 N NaCl.

Fig. 11   Bode-plots for Al 6061 with 10 vol% SiC during passivation in 5mM $CeCl_3$. Curve 1 - one day; Curve 2 - 7 days.

Table 1. Summary of Impedance Data for Passivation and Corrosion Tests[*] for Al 6061-T6 (degreased)

(R_p in $10^6 ohmcm^2$ and C_p in $\mu F/cm^2$)

I, $CeCl_3$

Conc(mM)	t_{pass}(d)	R_p(pass)	C_p(pass)	t_{corr}(d)	R_p(corr)	C_p(corr)
4	7	1.10	8.2	65	1.00	10.9
5	7	1.18	7.5	33	4.00	8.7
10	7	2.28	8.9	60	0.23	8.0
10	15	1.00	9.0	63	1.98	8.5
10	30	1.36	9.5	60	1.98	9.0
30	7	2.24	8.1	60	0.13	7.6
30	15	1.80	8.5	63	0.23	7.3
30	30	2.02	8.6	60	4.25	9.3

II, $LaCl_3$

Conc(mM)	t_{pass}(d)	R_p(pass)	C_p(pass)	t_{corr}(d)	R_p(corr)	C_p(corr)
4	7	n.d.	n.d.	68	2.25	10.4
10	7	1.43	6.9	60	0.10	8.4
10	15	4.70	7.3	63	0.13	13.7
10	30	0.02	11.8	21	0.06	10.1
30	7	1.40	7.6	60	0.09	9.5
30	15	0.48	7.9	63	0.14	14.7
30	30	0.38	9.1	60	0.19	11.0

[*] samples immersed in 0.5N NaCl, open to air.

n.d. : no data.

III, NdCl$_3$

Conc(mM)	t_{pass}(d)	R_p(pass)	C_p(pass)	t_{corr}(d)	R_p(corr)	C_p(corr)
10	7	2.60	9.7	42	1.70	10.1
10	15	0.80	8.6	63	0.95	9.5
10	30	0.76	10.0	60	3.52	8.9
25	7	1.60	8.5	60	0.13	8.0
25	15	1.41	8.3	63	0.16	8.3
25	30	1.52	7.9	60	0.50	9.8

IV, PrCl$_3$

Conc(mM)	t_{pass}(d)	R_p(pass)	C_p(pass)	t_{corr}(d)	R_p(corr)	C_p(corr)
10	7	1.01	8.5	60	4.00	10.0
10	15	1.78	9.8	62	3.62	9.5
10	30	0.56	12.1	60	0.33	10.9
25	7	2.52	8.0	60	1.02	8.8
25	15	0.59	7.5	62	1.52	8.9
25	30	0.59	7.5	60	0.60	8.6

V, CeCl$_3$ + NaNO$_3$

Conc(mM)	t_{pass}(d)	R_p(pass)	C_p(pass)	t_{corr}(d)	R_p(corr)	C_p(corr)
5(CeCl$_3$) 5(NaNO$_3$)	10	n.d.	n.d.	30	3.40	8.5
5(CeCl$_3$) 5(NaNO$_3$)	15	n.d.	n.d.	30	5.00	9.2

VI, Blank[+]

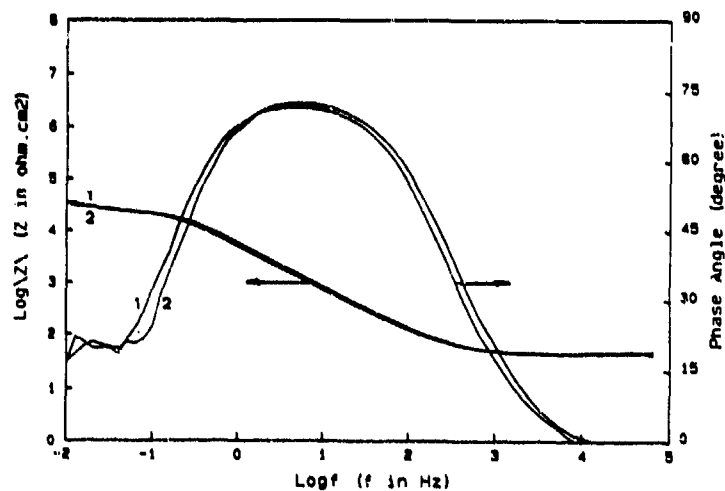| Conc(mM)	t_{pass}(d)	R_p(pass)	C_p(pass)	t_{corr}(d)	R_p(corr)	C_p(corr)
				3	0.032	12.8
				7	0.017	14.1

+ : untreated sample in 0.5N NaCl.

Fig. 12   Bode-plots for Al/SiC with 20 vol% SiC in 0.5 N NaCl after passivation in
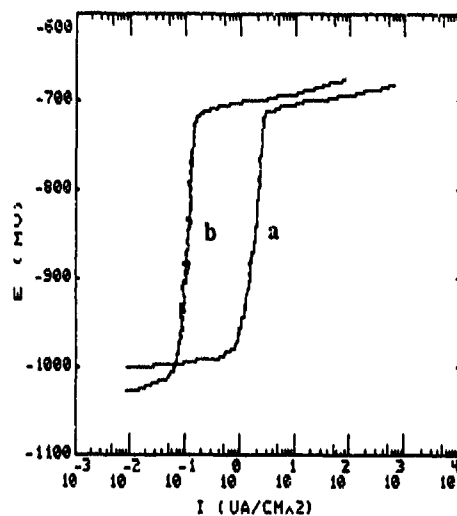5mM CoCl$_3$ for 7 days.   Curve 1 - one day; Curve 2 - 7 days.

Fig. 13   Anodic polarization curves of Al 6061-T6 in deaerated 0.5 N NaCl solution.
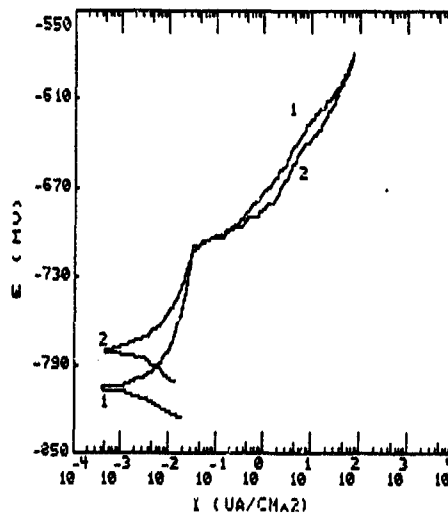Curve a - as-received sample; curve b - after 7 days passivation in CeCl$_3$.

Fig. 14   Anodic polarization curves of Al 6061-T6 in aerated 0.5 N NaCl after
passivation in 5mM CeCl$_3$ for 7 days.   Curve 1 - 1 day; Curve 2 - 60 days.

-12-

10 shows the use of EIS as a quality control tool for a commercial procedure (Alodine 600, Amchem) on Al 7075-T6 (15). A scatter band has been prepared based on the EIS-data for six samples which had been treated in the same manner. The three curves shown in Fig. 10 are for the mean M and +/- 2σ, where σ is the standard deviation. This scatter band is quite narrow except at the lowest frequencies, where the measurements were sometimes affected by drifts in the corrosion kinetics. The EIS-data for Al 6061 after chemical passivation in $CeCl_3$ (Fig. 5 and 6), $NdCl_3$ (Fig. 7) and $PrCl_3$ (Fig. 8) are very similar to those shown in Fig. 10 for the conversion coated Al 7075-T6 as far as the capacitive behavior in the entire frequency region and the high R_p-values are concerned. The capacitance is lower for the conversion coated surface due to the thicker surface layer and/or a higher dielectric constant. In making this comparison between the results obtained for the two different surface treatments, it has to be considered that the spectra in Fig. 5-8 were determined after several weeks, while the scatter band shown in Fig. 10 is for an exposure time of only 2 h.

Chemical passivation in 5 mM $CeCl_3$ was also applied to Al 6061/SiC with 10% or 20% SiC particulates. The impedance spectra for the Al/10% SiC MMC are shown in Fig. 11 for immersion in $CeCl_3$ at the beginning and at the end of the passivation process. R_p decreased during the passivation time from 0.6×10^6 ohm.cm^2 to 0.2×10^6 ohm.cm^2 indicating that the passivation was not as effective as for the wrought alloys. Spectra for exposure to NaCl are shown in Fig. 12 for Al/20%SiC. The transmission line-type impedance at the lowest frequencies (3-8) indicates that pitting was occurring. Visual observation confirmed the conclusion from the analysis of the impedance data that pits had initiated for both types of Al/SiC MMC during the first day of exposure to NaCl.

The results described in this section demonstrate the dramatic improvements of the corrosion behavior of Al alloys which can be achieved by simple immersion in REMCs such as $CeCl_3$, $NdCl_3$ or $PrCl_3$. However, even if the passivation time is lowered to 4 days (7), this is still too long for practical applications. In addition, the problems of providing the same degree of corrosion protection to the Al/SiC MMC make it necessary to evaluate in more detail the effects of the pre-existing surface structure on the efficiency of the passivation process. Therefore the effort was directed next to modifications of the passivation procedure which could allow processing in much shorter time periods while maintaining the same degree of corrosion resistance.

2.2.1.2   Polarization Data

Anodic Polarization Curves

Typical anodic polarization curves in deaerated 0.5 N NaCl are shown in Fig. 13 for as-received Al 6061 and for Al 6061 after passivation in 5 mM $CeCl_3$ for 7 days. Two very significant results can be observed from these two curves which are typical for the other passivation solutions. First, the passive c.d. i_{pass} decreased by more than a factor of ten due to passivation in $CeCl_3$ and second, the breakdown potential E_b did not change as a result of passivation. Polarization curves obtained in aerated NaCl also showed that E_b did not change as a result of chemical passivation and remained constant during immersion in NaCl for 60 days (Fig. 14). The observed difference between E_{corr} and E_b which decreases slightly with exposure time explains why pitting did not occur for the passivated samples during exposure to aerated NaCl.

Cathodic Polarization Curves

When the chemical passivation treatment was repeated for newly acquired Al 6061 material, problems were encountered with successful passivation of that material. A detailed investigation showed that the new sheet of Al 6061 contained a large number of defects which were mainly located in the rolling direction. Fig. 15a shows the surface of the material which was used in the initial studies, while Fig. 15b illustrates the types of defects which were exposed in the newly acquired sheets of Al 6061. In the course of this investigation it was discovered that cyclic potentiodynamic polarization curves were a very sensitive indicator of the quality of the as-received surfaces (17). For as-received surfaces with a uniform oxide film as shown in Fig. 15a, the cyclic polarization curves had a very simple shape as shown in Fig. 16 for passivation in 5 mM $CeCl_3$ for 2 h. For an as-received surface with pre-existing defects the shape of the polarization curve was very different as shown in Fig. 17 for passivation times of 2 h (curve 1) and 7 days (curve 2) in the same solution. Very similar results have been obtained for the two types of surface in the other REMC solutions (17).

Important information concerning the surface properties before and after passivation can be obtained from the polarization curves of the two different types shown in Fig. 16 and 17. An analysis of the results for different passivation solutions and passivation times is given in Tables 2 and 3. The data in Table 2 are for uniform as-received surfaces. $E_{corr,1}$ is the corrosion potential at the beginning of the scan, while $E_{corr,2}$ is the potential at which the current reverses its sign in the reverse sweep. No significant differences in the potential or the value $\Delta E = E_{corr,2} - E_{corr,1}$ can be detected. However, it was found that the limiting c.d. for oxygen reduction i_{1im} decreased with increasing degree of corrosion protection provided by chemical passivation. As shown in Table 2, i_{1im} had the lowest values for passivation in $CeCl_3$ and $NdCl_3$, while i_{1im} for the $PrCl_3$ treatment was about twice as high. For treatment in YCl_3 which, according to the impedance data in Fig. 9 did not provide a very protective surface, a much higher i_{1im} is recorded; however, this value is still only one half of that for the untreated surface. The reduction of i_{1im} by chemical passivation suggests that the modified surface provides an additional barrier for the reduction of oxygen. Since i_{1im} equals i_{corr} for a diffusion controlled process, the efficiency of the passivation treatments can be ranked in terms of i_{1im} which leads to:

$$CeCl_3 > NdCl_3 > PrCl_3 > YCl_3 \gg \text{as-received.}$$
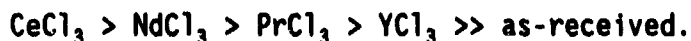
The shape of the return sweep is quite different for the surfaces with pre-existing defects as shown in Fig. 17. A shoulder occurs at about the potential where $E_{corr,2}$ was located for samples with uniform surface oxides (Fig. 16). The sweep continues and reaches $E_{corr,2}$ at much more negative values than those given in Table 2. The coordinates of the shoulder (point A in Fig. 17) are given as E_{pp} and i_{pp} in Table 3. It is assumed that the potential region between point A and $E_{corr,2}$ corresponds to repassivation of the pre-existing defects. With increasing exposure time to the passivating solutions $E_{corr,2}$ becomes more negative and i_{pp} increases (Table 3). This is probably due to continuing attack of the chloride ions of the passivating solution at the defects.
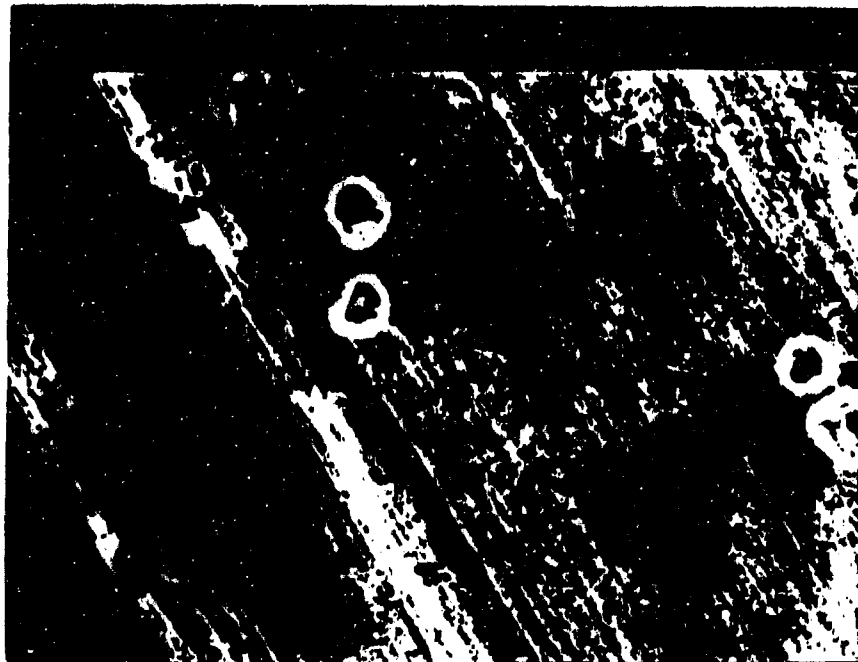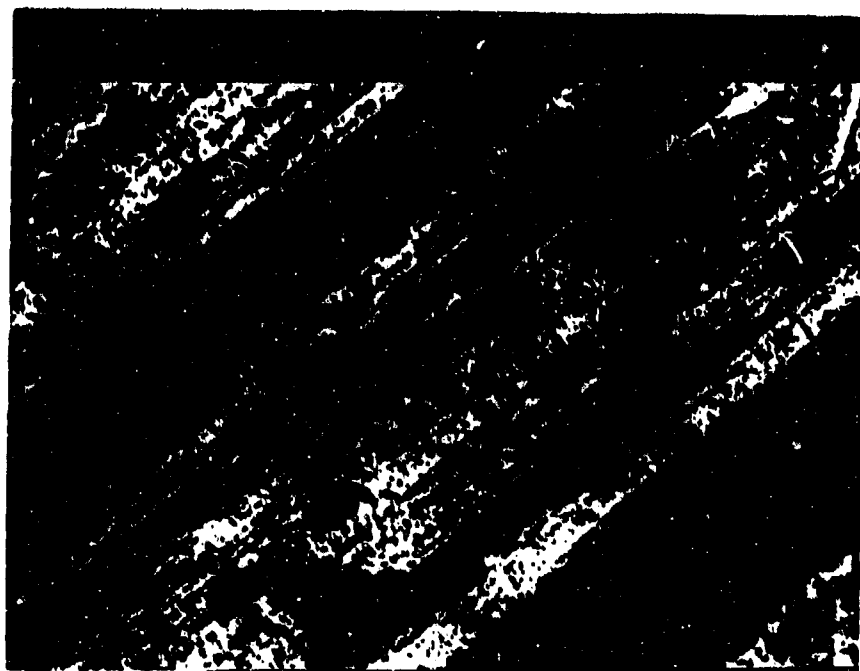
Fig. 15   SEM analysis of as-received Al 6061-T6. (a) Sample with
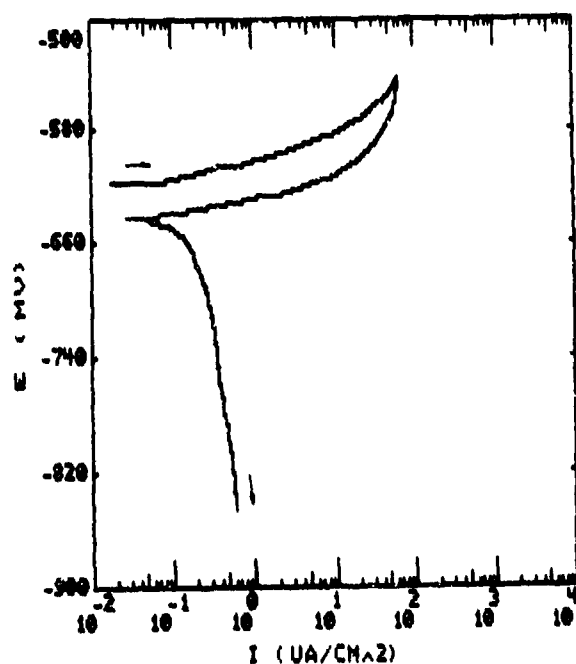an uniform oxide film. (b) Sample with surface defects.

Fig. 16 Cyclic Polarization curve in 5mM CeCl$_3$ for as-received for Al 6061-T6 with a uniform pre-existing oxide film after 2 hours passivation.
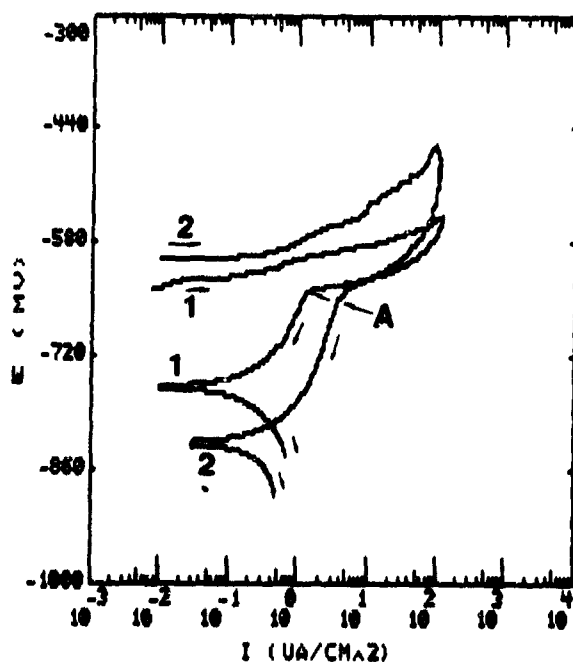

Fig. 17 Cyclic Polarization curves in 5mM CeCl$_3$ for as-received Al 6061-T6 with surface defects after 2 hours (curve 1) and 7 days (curve 2) passivation.

Table 2 Cyclic Polarization Data for Al 6061-T6
with a uniform Aluminum Oxide Film

passivation solution (5 mM)	t_{pass} (h)	$E_{corr,1}$ (mV)	$E_{corr,2}$ (mV)	ΔE^+ (mV)	i_{lim}^* ($\mu A.cm^{-2}$)
blank[++]	2h	-620	-642	-22	4.50
CeCl$_3$	2h	-618	-642	-24	0.55
NdCl$_3$	2h	-618	-650	-32	0.63
PrCl$_3$	2h	-618	-646	-28	1.06
YCl$_3$	2h	-614	-662	-48	2.16

+: $\Delta E = E_{corr,2} - E_{corr,1}.$

*: At -850 mV (SCE).

++: 5 mM NaCl.

Table 3. **Cyclic Polarization Data during Chemical Passivation of Al 6061-T6 without a Uniform Aluminium Oxide Film**

passivation solution (5 mM)	t_{pass} (h)	$E_{corr,1}$ (mV)	$E_{corr,2}$ (mV)	ΔE^+ (mV)	E_{pp} (mV)	i_{pp} (μAcm^{-2})
blank	2h	-602	-780	-165	-615	2.5
blank	7d	-600	-842	-232	-613	3.9
$CeCl_3$	2h	-645	-762	-120	-642	1.3
$CeCl_3$	7d	-610	-824	-188	-636	3.8
$NdCl_3$	2h	-635	-730	-106	-624	1.7
$NdCl_3$	7d	-649	-824	-212	-612	4.1
$PrCl_3$	2h	-625	-756	-126	-630	2.2
$PrCl_3$	7d	-639	-852	-216	-636	5.8
YCl_3	2h	-635	-860	-220	-640	1.8
YCl_3	7d	-649	-828	-208	-620	2.6

+ : $\Delta E = E_{corr,2} - E_{pp}$.

2.2.1.3   Surface Analysis

Fig. 18 shows the surfaces of Al 6061 with a uniform as-received oxide film after chemical passivation in 10 mM $CeCl_3$ (Fig. 18a) or $NdCl_3$ (Fig. 18b). Ce and Nd, respectively, were detected in the modified surface layers by EDAX. For samples with uniform as-received oxide films which have been passivated in 10 mM $CeCl_3$ (Fig. 19a) or 30 mM $CeCl_3$ (Fig. 19b) for 14 days no pits were detected by SEM after exposure to NaCl for 60 days (Fig. 19). Similar results have been obtained for samples which had been passivated in $NdCl_3$ or $PrCl_3$. For the treatment in $LaCl_3$ or YCl_3 EDAX documented the presence of La and Y in the modified surface layers, however pits and corrosion products were observed after exposure to NaCl for 60 days (Fig. 20).

Auger electron spectroscopy (AES) was used to analyze the composition of the modified surface of Al 6061 after immersion in 5 mM $CeCl_3$ for 7 days. A typical AES spectrum is shown in Fig. 21. Ce peaks can clearly be detected. The concentration profile for oxygen, Ce and Al is given in Fig. 22. A high atomic concentration of Ce (37.5%) was detected at the outside layer of the modified surface, the thickness of which was determined to exceed 1500 A.

2.2.1.4   Weight Loss Measurements

The corrosion rate data listed in Table 4 reflect the trends for the EIS-data in Table 1. For samples with passivation in 10 or 30 mM $CeCl_3$, 10 mM and 25 mM $PrCl_3$ for times between 7 and 30 days, corrosion rates determined after exposure to NaCl based on weight loss data were less than 0.1 mg/dm^2.d(mdd), while for samples passivated in 25 mM $NdCl_3$ corrosion rates ranged from 0.1 to 0.2 mdd. Corrosion rates increased with increasing passivation time in 10 mM $LaCl_3$. It will be noted that even for the less effective treatments such as $LaCl_3$, corrosion rates for exposure times of two months were only about 1% of those for the untreated samples after one week exposure to NaCl. Based on weight loss data the corrosion resistance produced by chemical passivation decreased in the following order:

$$CeCl_3 > PrCl_3 > NdCl_3 > LaCl_3 >> \text{as-received}$$
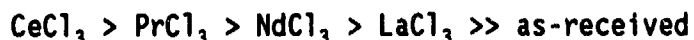
2.2.2   Passivation in $CeCl_3$/$Ce(NO_3)_3$

In an attempt to shorten the passivation time, pure Al and Al 6061 were passivated first in 5 mM $Ce(NO_3)_3$ and then in 5 mM $CeCl_3$ at 100°C for 2 h. A mixture of $CeCl_3$ and $Ce(NO_3)_3$ was also used. In order to produce a uniform oxide film before passivation, the surfaces were first deoxidized and then baked at 100°C at high humidity levels for at least 24 h. As the EIS-data for Al 6061 which were obtained during passivation in the mixed solution show the modified surface was very corrosion resistant (Fig. 23).

The impedance spectra obtained for pure Al and Al 2024 which had been passivated in $Ce(NO_3)_3$ and then in $CeCl_3$ as discussed above are shown for exposure to NaCl in Fig. 24. Curve 1 is for the passivated pure Al, while curve 2 is for the untreated surface after 3 days exposure to NaCl. The superior corrosion resistance of the passivated surface becomes evident from a comparison of these two curves. Two time constants and pitting were observed after one day for the untreated surface and also for the passivated Al 2024 (curve 3).
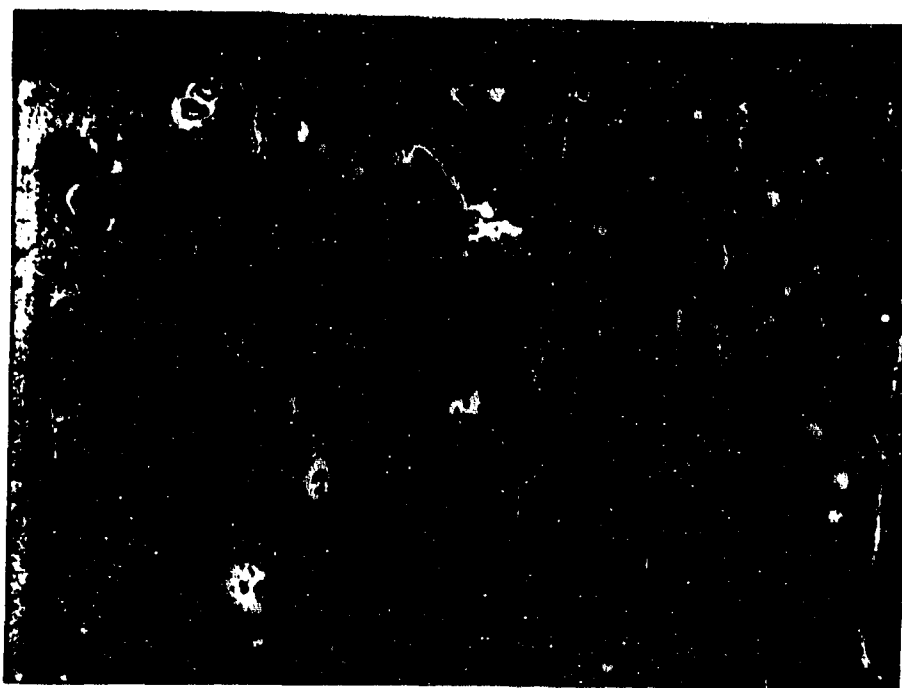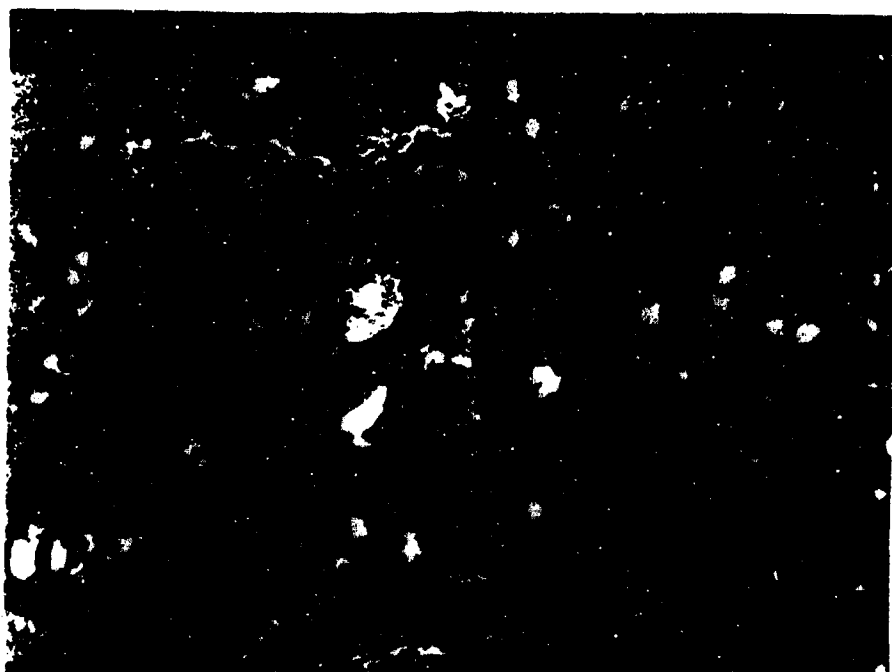
Fig. 18   SEM analysis of Al 6061-T6 after chemical passivation
(a) 10mM CeCl$_3$ for 7 days; (b) 10mM NdCl$_3$ for 7 days.
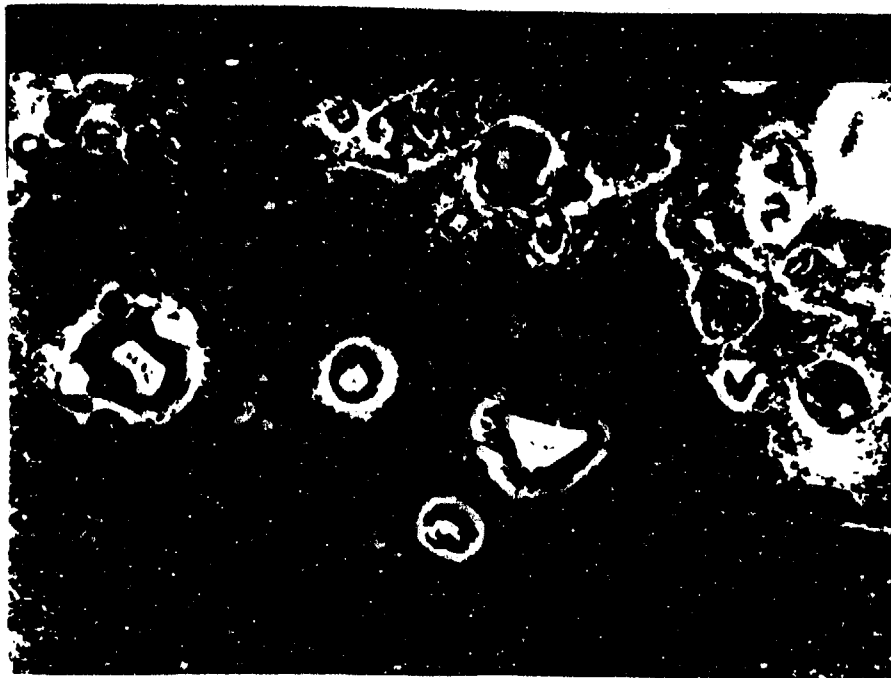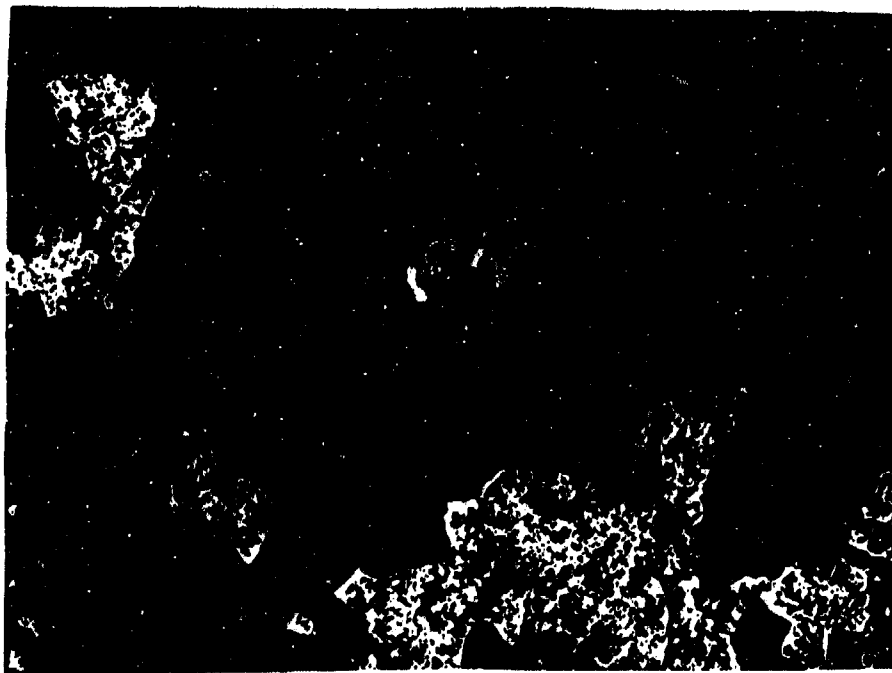
a

b

Fig. 19   SEM analysis of Al 6061-T6 after chemical passivation
          and explsure to 0.5 N NaCl for 60 days.   (a) 10mM CeCl$_3$
          for 14 days; (b) 30mM CeCl$_3$ for 14 days.

a

b

Fig. 20 SEM analysis of Al 6061-T6 after chemical passivation
in LaCl$_3$ for 14 days and exposure to 0.5 N NaCl for
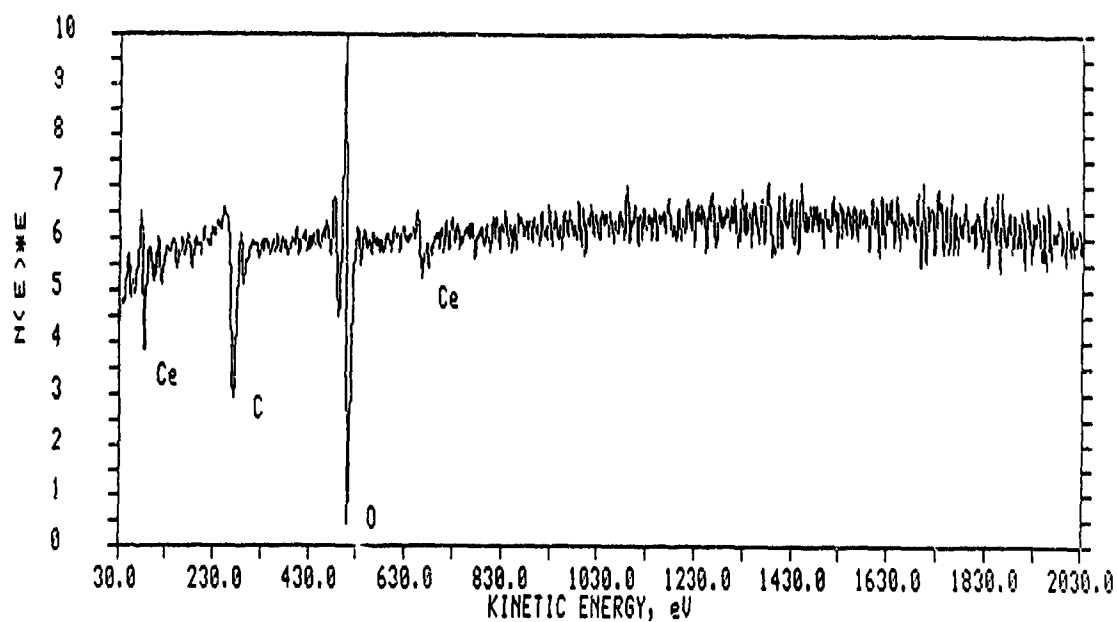60 days. (a) 10mM LaCl$_3$; (b) 30mM LaCl$_3$.

Fig. 21   AES spectrum for Al 6061-T6 after passivation
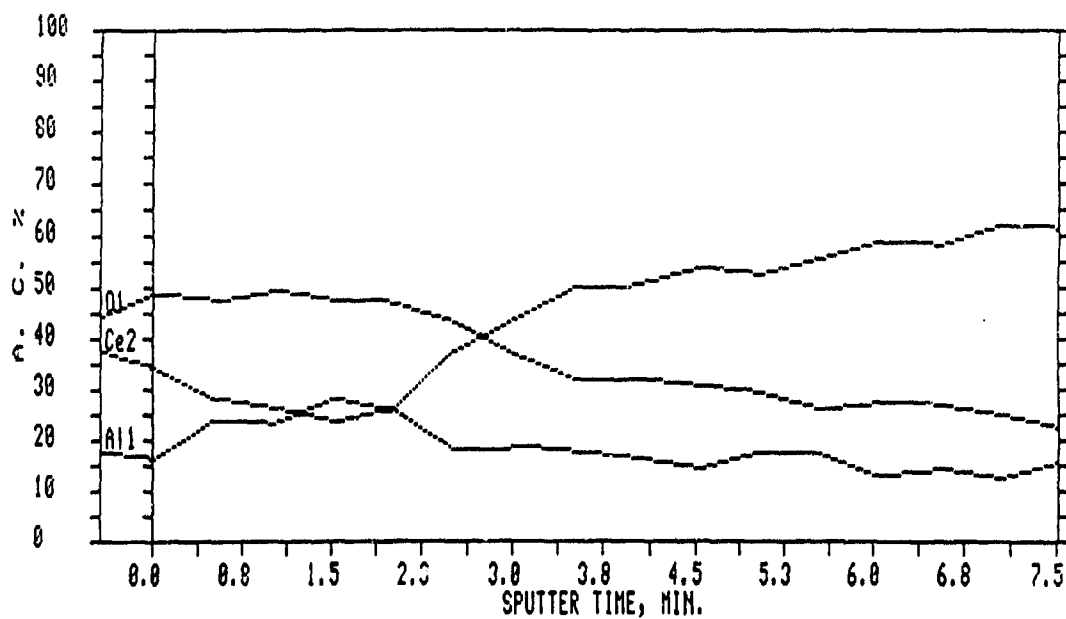   in 5mM CeCl₃ for 7 days.

Fig. 22   AES concentration profile for Al 6061-T6 after passivation
           in 5mM CeCl₃ for 7 days.

Table 4 Summary of Weight Loss Data [+]

1. CeCl$_3$

Conc(mM)	t_{pass}(day)	t_{corr}(day)	Corrosion Rate (mg/day.dm^2)
10	7	60	0.07
10	15	63	0.03
10	30	60	0.02
30	7	60	-0.02
30	15	63	-0.00
30	30	60	-0.01

2. NdCl$_3$

Conc(mM)	t_{pass}(day)	t_{corr}(day)	Corrosion Rate (mg/day.dm^2)
10	7	42	-0.02
10	15	63	-0.08
10	30	60	0.00
25	7	60	0.13
25	15	63	0.13
25	30	60	0.20

3. PrCl$_3$

Conc(mM)	t_{pass}(day)	t_{corr}(day)	Corrosion Rate (mg/day.dm^2)
10	7	60	0.02
10	15	62	0.03
10	30	60	0.15
25	7	60	-0.16
25	15	62	0.03
25	30	60	0.05

4. LaCl$_3$

10	7	60	0.13
10	15	63	0.16
10	30	21	1.05
30	7	60	0.29
30	15	63	0.10
30	30	60	0.13

5. Blank*

	3	11.50
	7	8.41

+ Negative values correspond to a weight gain.

* As-received Al 6061-T6 (degreased only).
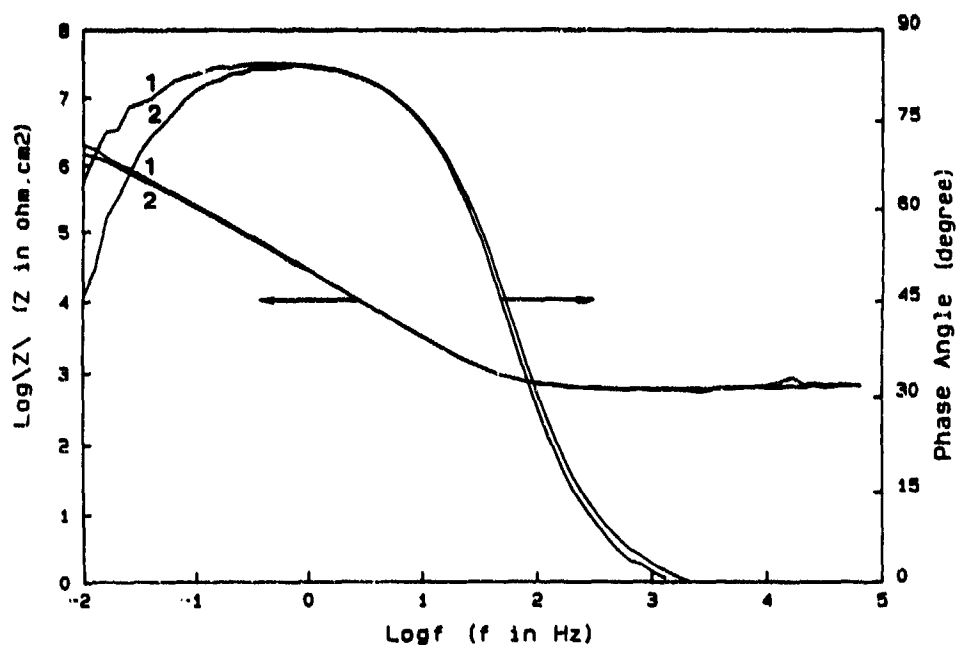
Fig. 23   Bode-plots for as-received Al during passivation in 5mM $CeCl_3$ + 5mM $Ce(NO_3)_3$ for one day (curve 1) and 7 days (curve 2).
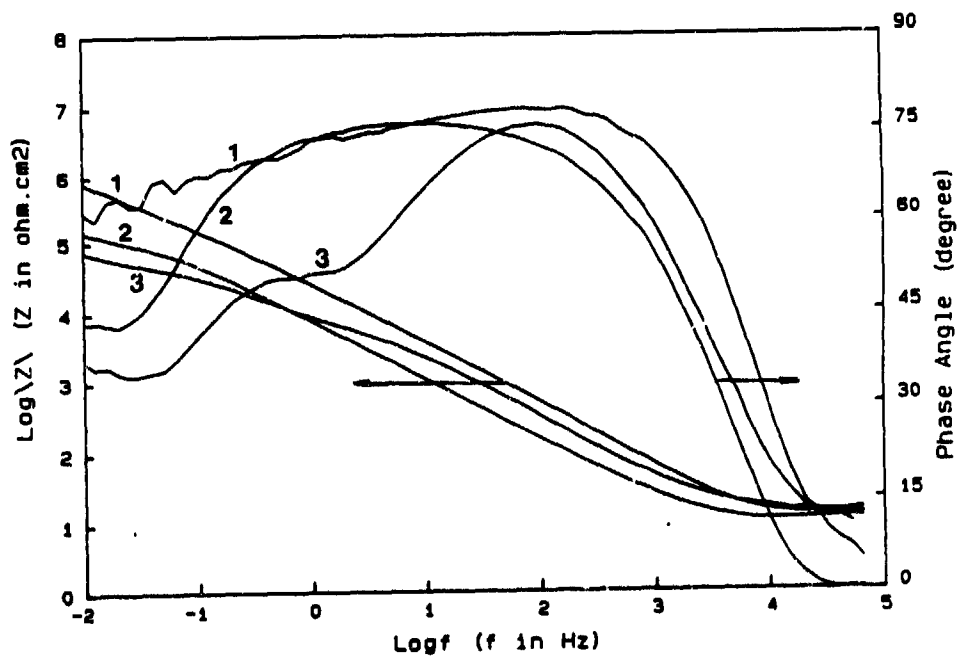

Fig. 24   Bode-plots for pure Al and Al 2024 in 0.5 NaCl with or without chemical passivation. Curve 1 - Pure Al after 2h passivation in 5mM $CeCl_3$ and in 5mM $Ce(NO_3)_3$ at 100°C for 2h, exposure to 0.5 N NaCl for three days. Curve 2 - Pure Al, untreated, in 0.5 N NaCl for 3d. Curve 3 - Al 2024 after 2h passivation in 5mM $CeCl_3$ and in 5mM $Ce(NO_3)_3$ at 100°C for 2h, exposure to 0.5 N NaCl for one day.

The results for pure Al, Al 6061 and Al 2024 obtained by passivation in Ce salt solutions at higher temperatures suggest that it is possible to shorten the passivation time considerably. However, there is a marked effect of alloy composition (Al 6061 vs. Al 2024) and probably also surface condition before passivation. It was considered necessary, therefore, to add an additional step to the passivation procedure. Attention was given to the use of molybdate solutions in the next phase of this program.

2.2.3 Passivation in Na_2MoO_4

A typical anodic polarization curve for Al 6061-T6 in 0.1 M Na_2MoO_4 is shown in Fig. 25, where E_{corr} = -1000 mV and a wide passive range extends from -800 mV to +1600 mV. Using the procedure described by Shaw et al. (12), Al 6061 was polarized in deaerated 0.1 M Na_2MoO_4 at E_{corr} + 300 mV for 2 h. A bright and uniform film was formed at the surface. However, during immersion in NaCl this film disappeared and pitting corrosion occurred. Fig. 26 shows the surface morphology after 24 h immersion in NaCl. Similar results were obtained for pure Al and Al 6061 for passivation at potentials between E_{corr} + 300 mV and E_{corr} + 500 mV. It was concluded that the procedure by Shaw et al. (12) might lead to a temporary increase of E_b, however long lasting corrosion protection as that obtained by immersion in REMCs was not possible.

Additional tests were performed with Al 6061-T6 which was immersed in aerated 0.1 M Na_2MoO_4 for 2 h at E_{corr}. An anodic potential scan showed that E_b had become 400 mV more positive than E_{corr}. However, when a sample which had been prepared in the same manner was immersed in NaCl, pitting occurred within 24 h. As before, the film formed in the molybdate solution dissolved in the aerated NaCl solution.

2.2.4 Passivation in $CeCl_3/Ce(NO_3)_3$ Followed by Na_2MoO_4 Treatment

The final surface modification procedure investigated in this program was a combination of chemical passivation in $CeCl_3$ + $Ce(NO_3)_3$ followed by an electrochemical step in Na_2MoO_4. The pretreatment of all samples consisted of deoxidizing and baking at 100 °C as described above. The passivation treatment in $CeCl_3$ + $Ce(NO_3)_3$ was then applied followed by anodic polarization in deaerated 0.1 M Na_2MoO_4 at + 500 mV vs SCE for 2 h.

Very corrosion resistant surfaces were obtained for Al 6061 by the $Ce(NO_3)_3/CeCl_3/Na_2MoO_4$ process. Fig. 27 gives a comparison of the spectra for an as-received surface, for which pitting is indicated by the impedance spectrum, and a treated surface, for which the spectrum is capacitive indicating that the corrosion rate is very low even after exposure for 30 days and localized corrosion did not occur in this time period. Fig. 28 shows that the spectra for the modified surface did not change during exposure to NaCl for 30 days which indicates that the modified surface is very stable even in an aggressive medium such as NaCl open to air. R_p exceeded 10^7 ohm.cm^2 during the entire corrosion test and localized corrosion was not observed for 60 d.

Table 5 gives a summary of the analysis of the EIS-data for as-received and passivated samples which had been exposed to NaCl for different time periods. For the untreated samples R_p remains about 4×10^4 ohm.cm^2 during 30 d exposure and the total capacitance which is due mainly to the capacitance of pits is about 7.7 μF/cm^2. For the combined treatment in cerium and molybdate solutions, pits
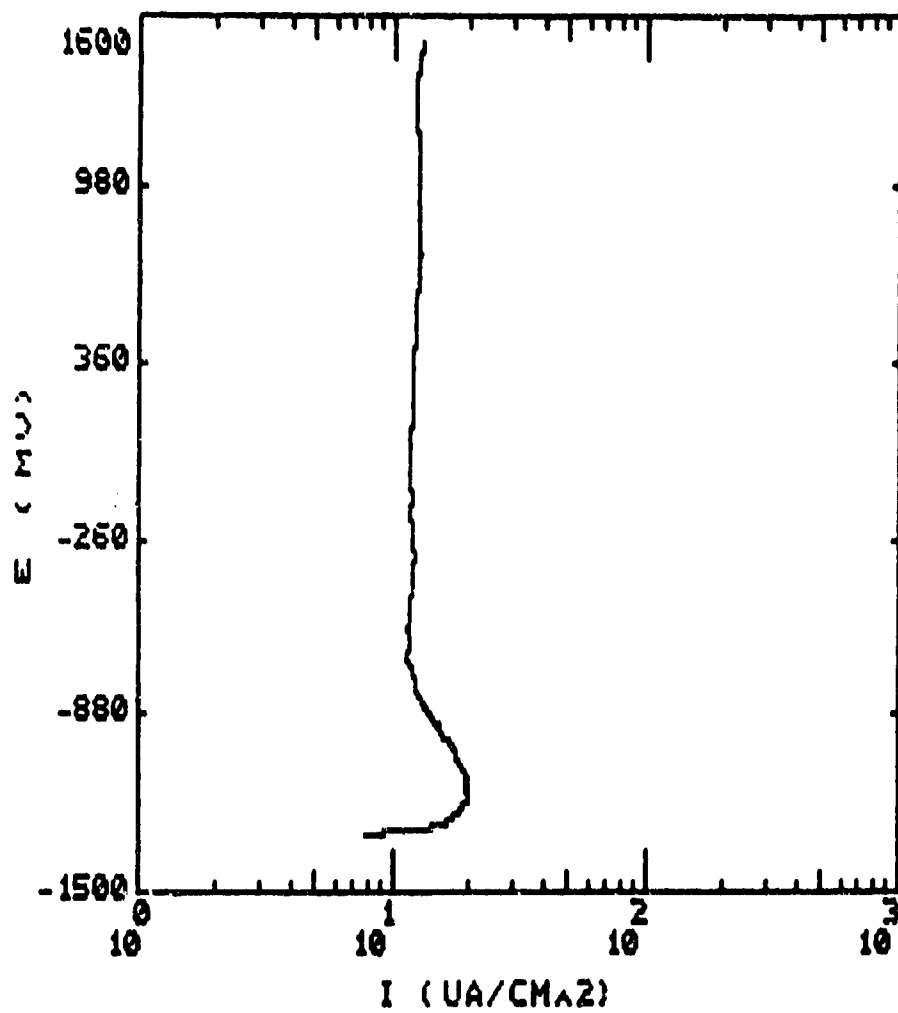
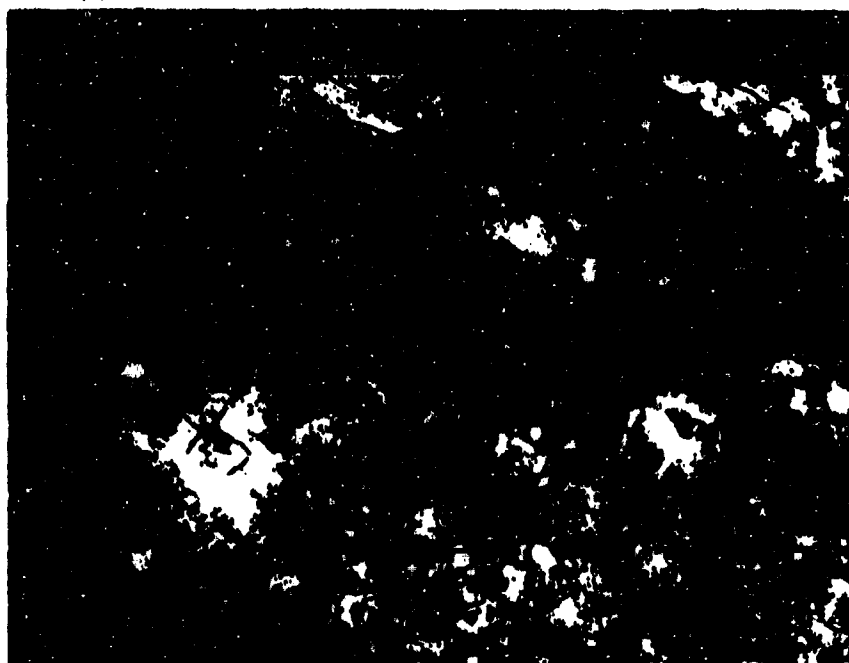Fig. 25 Anodic polarization curve of Al 6061-T6 in
aerated 0.1 M Na₂MoO₄.

Fig. 26 SEM analysis of Al 6061-T6 after exposure to
0.5 N NaCl for one day; passivated by anodic
polarization in 0.1 M Na_2MoO_4 at 300 mV vs
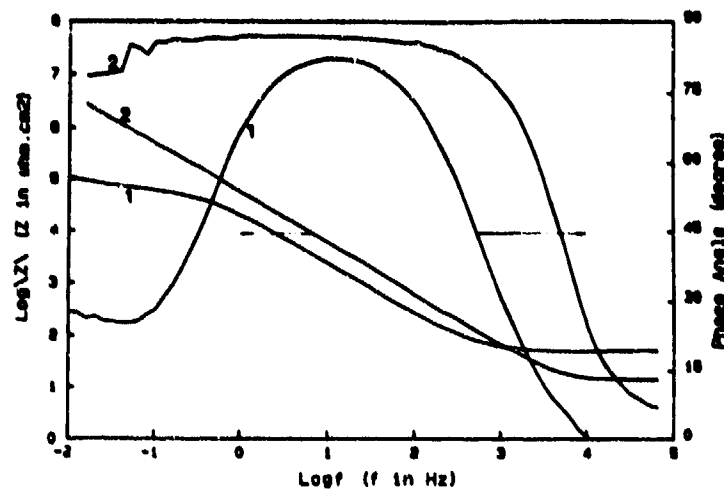E_{corr} for 2h.

Fig. 27   Bode-plots for Al 6061-T6 after 30d in 0.5 N NaCl.
           Curve 1 - as-received; Curve 2 - Ce + Mo passivation.
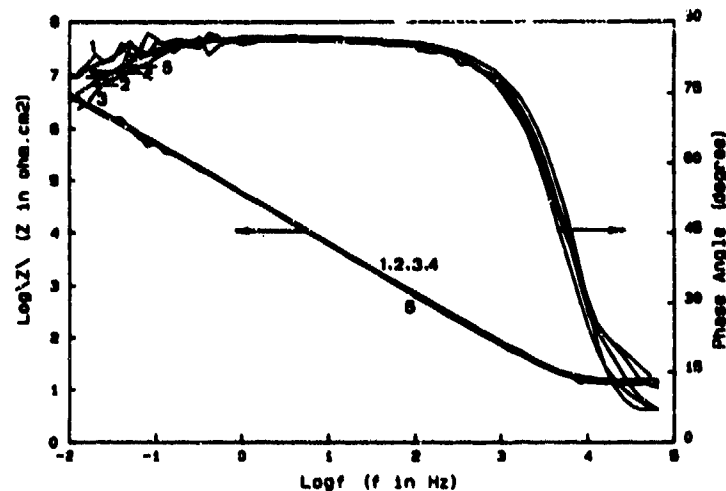

Fig. 28   Bode-plots of Al 6061-T6 in 0.5 N NaCl after Ce + Mo
           passivation. Curve 1 - 6h; Curve 2 - 1d; Curve 3 - 7d;
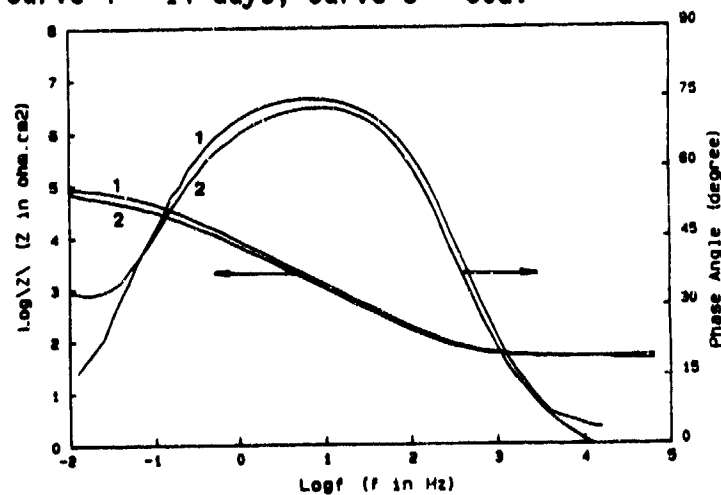   Curve 4 - 14 days; Curve 5 - 30d.

Fig. 29   Bode-plots for Al 6061/SiC in 0.5 N NaCl after passivation
           in $CeCl_3$ and $Ce(NO_3)_3$ for 4 hours; Curve 1 - 1d; Curve 2 - 7d

Table 5 Analysis of Impedance Spectra Obtained
for Al 6061 during Exposure to 0.5N NaCl (aerated)

	R_p $(10^6$ ohm.cm$^2)$	C_t (uF/cm^2)	C_p (uF/cm^2)
1. as-received			
1 d	0.05	7.5	
2 d	0.05	7.7	
7 d	0.04	7.7	
14 d	0.04	7.7	
30 d	0.04	7.9	
2. with Ce+Mo treatment			
6 h	18.5		3.3
1 d	17.9		3.3
7 d	16.8		3.4
14 d	16.4		3.3
30 d	16.0		3.6

did not initiate in 60 d and R_p was about 1.7×10^7 ohm.cm^2 and C_p was about 3.3 $\mu F/cm^2$.

For Al 2024 and Al/SiC this passivation procedure was not as successful as for Al 6061. For Al 2024 pitting occurred after one day exposure to NaCl. For Al/SiC pitting was first observed visually after 7 days. At this time the EIS-data (Fig. 29) also showed the typical low-frequency behavior which is associated with localized corrosion (3-8).

Since the impedance data shown in Fig. 27-29 had indicated that the combined Ce/Mo treatment could enhance the already excellent resistance to localized corrosion, dc polarization data were obtained to determine the mechanism by which the addition of the Mo treatment increases the corrosion resistance. Curve 1 in Fig. 30 is the typical anodic polarization curve for untreated Al 6061 in aerated NaCl, where $E_{corr} = E_b$. Dramatic changes are observed for the sample which had been treated in addition by anodic polarization in the molybdate solution as described above. E_{corr} had shifted to -485 mV, E_b was -325 mV and i_p was less than 0.003 $\mu A/cm^2$. The value of i_p is three orders of magnitude lower than that reported by Shaw et al. (12) and was below the lower limit of the PAR model 173 potentiostat. After immersion in NaCl for one month, E_{corr} had shifted to -691 mV and E_b had decreased to -534 mV which meant that the difference between these two potentials had not changed.

An anodic polarization curve was measured for the passivated sample which had been exposed to NaCl for one month. A very unusual polarization curve was obtained (Fig. 31). Initially, only a very small passive c.d. i_p which is below the detection limit of the potentiostat was recorded. When E_b was reached, the current increased and a polarization curve with an active/passive transition and wide passive region was obtained. After this test, microscopic observation showed that one very small pit had developed, while the remainder of the surface was completely unattacked. Apparently, the polarization curve in Fig. 31 is that of this single pit. To our knowledge, a polarization curve such as that shown in Fig. 31 for passivated Al 6061 has never been reported before. The passive film formed in the combined Ce/Mo treatment is quite different from that formed in the Ce or Mo treatment alone. The very low i_p and very high E_b suggest that the goal of developing a "stainless aluminum" can be reached by the Ce/Mo treatment and its further refinements.

Recording of a cathodic polarization curve in 0.5 N NaCl showed that the oxygen reduction reaction is also much slower on the modified surface (Fig. 32). The value of i_{lim} at -850 mV vs SCE is 1.6 $\mu A/cm^2$ for the passivated surface. Apparently, the modified surface does not allow either oxydation or reduction processes to occur at any appreciable rates and shows the behavior which is typical of insulators.

EDAX analysis showed the presence of both Ce and Mo in the modified surface layers (Fig. 33). Observation by SEM of the sample for which the polarization curve in Fig. 31 had been obtained provided some surprising results since it proved very difficult to find the area(s) where breakdown due to anodic polarization had occurred. Fig. 34 shows the only spots where very small pits had developed.
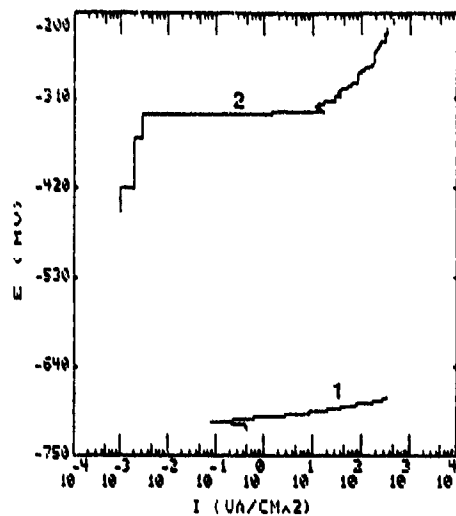
Fig. 30   Anodic polarization curves for Al 6061-T6 in aerated 0.5 N NaCl; Curve 1 - as-received sample;
Curve 2 - after passivation in 5mM CeCl$_3$ + 5mM Ce(NO$_3$)$_3$ for 4 hours and anodic polarization
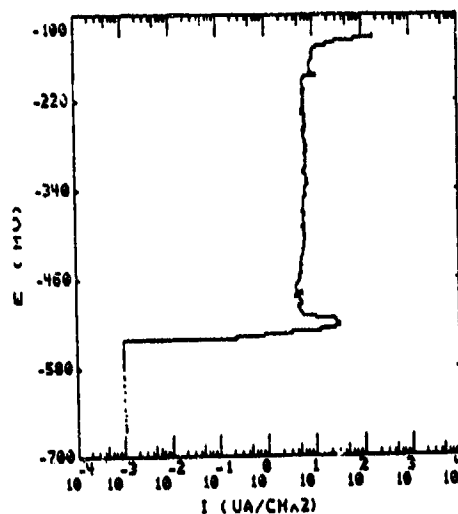in 0.1 M Na$_2$MoO$_4$ for 2h.

Fig. 31   Anodic polarization curve for passivated Al 6061-T6 after exposure to aerated 0.5 N NaCl
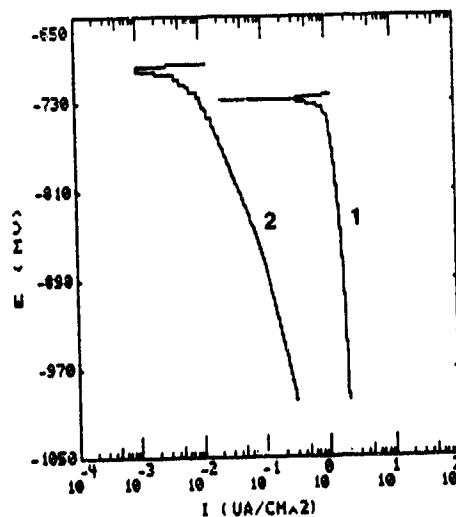for 30 days.

Fig. 32   Cathodic polarization curves for Al 6061 in 0.5 N NaCl. Curve 1 - as-received sample;
Curve 2 - after passivation in CeCl$_3$/Ce(NO$_3$)$_3$ Na$_2$MoO$_4$.
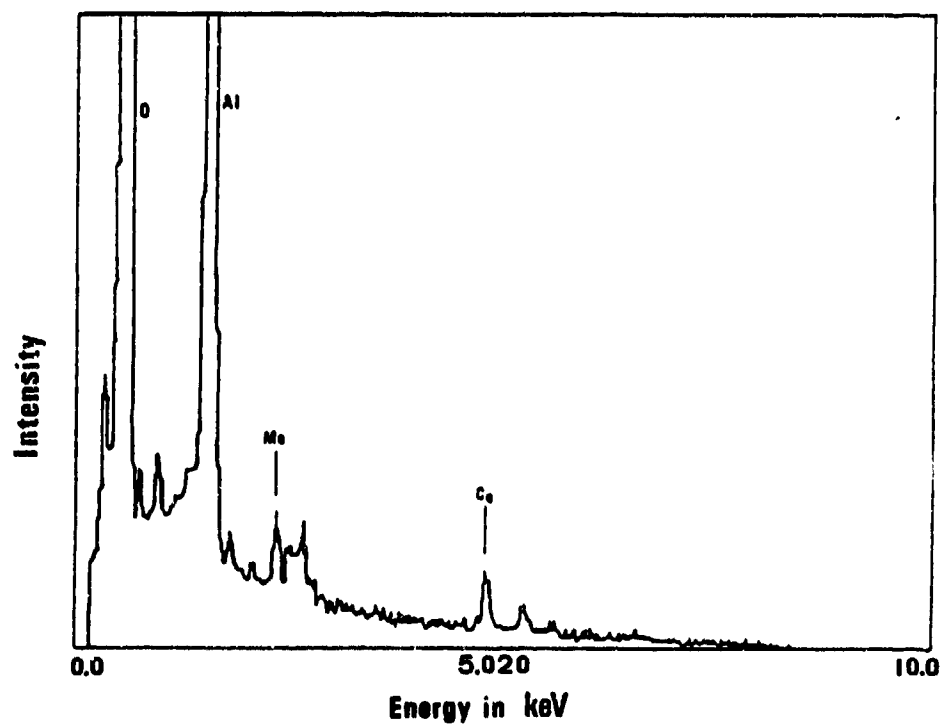
Fig. 33   EDAX analysis of Al 6061-T6 after Ce + Mo passivation.

Fig. 34   SEM analysis of Al 6061-T6 with Ce + Mo passivation
           followed by anodic polarization; exposure to aerated
           0.5 N NaCl for 30 days followed by anodic polarization.

The modified surface layers produced by the Ce/Mo treatment have also been analyzed by AES (Fig. 35). The concentration profile (Fig. 36) shows that Ce is present in fairly large amounts, while the concentration of Mo is apparently quite low. It is possible that most of the Mo is located in the outermost layers of the surface film and is therefore very difficult to detect in the sputtering process.

2.2.5 AC Passivation

Difficulties with the application of chemical passivation in its various forms discussed here were observed with Al 2024 which is one of the least corrosion resistant Al alloys due to its high Cu content. An ac passivation procedure was designed with the purpose of reducing the Cu content of the Al 2024 surface before passivation and thereby eliminating the Al/Cu couple which seems to interfere with the passivation process. A potential square wave between -520 mV and -640 mV was applied to Al 2024 for 3 d during exposure to 5 mM $CeCl_3$ followed by a square wave between -610 mV and -640 mV for another 3 d. The modified surface did not pit during exposure to NaCl for 35 d which is a very encouraging result. Based on the results obtained for Al 2024 in this program, it can be concluded that ac passivation is a very promising approach for the passivation of the less corrosion resistant Al alloys such as Al 2024 or Al 7075 in the T73 condition (15).
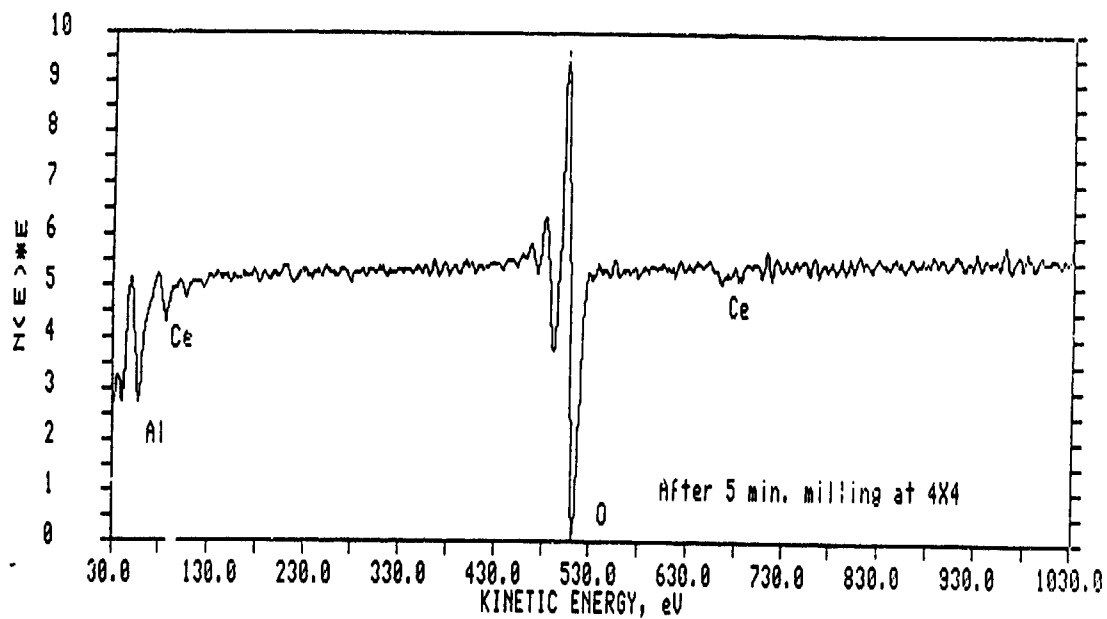
Fig. 35 AES spectrum for Al 6061-T6 with Ce + Mo passivation and
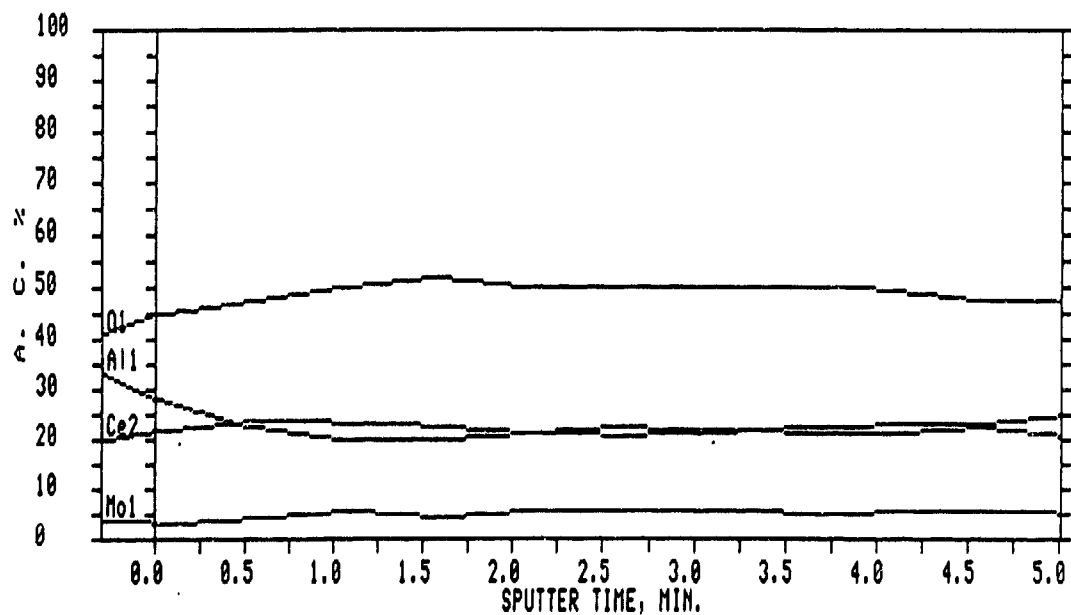exposure to 0.5 N NaCl for 30 days.

Fig. 36 AES concentration profile for Al 6061 with Ce + Mo
passivation and exposure to 0.5 N NaCl for 30 days.

3.0 SUMMARY AND CONCLUSIONS

Immersion of Al alloys in solutions of rare earth metal chlorides such as $CeCl_3$, $NdCl_3$ or $PrCl_3$ has produced significant improvements of the resistance to localized corrosion. Based on weight loss and EIS data it was concluded that the corrosion resistance of Al 6061-T6 produced by chemical passivation decreased in the order:

$$CeCl_3 > PrCl_3 > NdCl_3 > LaCl_3 >> \text{as-received.}$$

This approach was less successful for Al/SiC MMCs where crevice corrosion was observed. Due to this problem and the long immersion times between 4 and 7 days the chemical passivation process was modified by increasing the temperature of the passivation solution and shortening the passivation time.

Initially, surface modification was attempted in boiling solutions of 5 mM $CeCl_3$ or $Ce(NO_3)_3$ or a mixture of these two solutions. The total passivation time was 4 h. Improvements in the corrosion resistance were obtained for pure Al and Al 6061. An electrochemical step was added in which the sample was polarized anodically in deaerated 0.1 M Na_2MoO_4 for 2h. Excellent resistance to localized corrosion was observed and pits did not initiate in 60d exposure of Al 6061 to NaCl. The polarization step alone did not produce lasting improvement of the corrosion resistance. Less satisfactory results have been obtained for Al/SiC and Al 2024. For the latter material, some attempts were made to use an ac passivation process. Preliminary results were encouraging.

Surface analysis by SEM/EDAX and AES showed the presence of Ce in the modified surface layers. It was more difficult to detect the presence of Mo which is either incorporated in very small amounts or only in the outer layers of the modified surface.

The results obtained with electrochemical dc techniques suggest that the surfaces formed in the Ce/Mo process do not support oxidation or reduction processes to any significant extent. This unique property of the modified surface layers can explain their excellent corrosion resistance. Even if the modified surface is damaged, it is unlikely that corrosion will occur in a scratch to any significant extent since the surrounding area does not act as a cathode which will drive the corrosion reaction of the anode. This conclusion needs to be verified in further research.

The results obtained in the project form an excellent basis for the development of "satinless aluminum" and the replacement of chromate conversion coatings with those produced by other non-toxic processes. Suggestions for further research are made in the following.

4.0 SUGGESTIONS FOR FURTHER RESEARCH

In further research, attempts should be made to optimize the procedures developed previously and continue the search for a "stainless aluminum". In addition, the ac passivation process which was quite successful for Al 2024 should be developed further. Special attention should be paid to metal matrix composites such as Al/SiC, for which problems with successful passivation had been encountered in the previous project, Al/Al$_2$O$_3$ and Al/graphite. Samples which had been processed with the optimum passivation procedures should be exposed in standard corrosion tests such as the salt spray test and in atmospheric corrosion tests in order to allow a comparison with the known behavior of samples which had been processed with the present standard procedures.

Mechanistic studies of modified surfaces which had been processed by the optimized procedures should be carried out using surface analysis techniques such as SEM/EDAX for an evaluation of the surfaces after corrosion tests and AES and XPS for the determination of the chemical composition and structure of the modified surface films. Electrochemical dc and ac techniques have been found to be very useful to follow the corrosion behavior during the corrosion tests and to evaluate the changes due to surface modification of the kinetics of the anodic and cathodic reactions which determine the corrosion behavior. System specific properties such as the values of the pitting potential, corrosion potential, passive current density and corrosion rate need to be determined for modified surfaces of materials such as Al 6061, Al 5XXX, Al 2024, Al/SiC, Al/Al$_2$O$_3$ and Al/graphite.

5.0 PUBLICATIONS AND PRESENTATIONS

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2. F. Mansfeld, H. Shih, and Y. Wang, "Improved Corrosion Resistance of Al Alloys by Surface Modification," 178th Meeting of The Electrochem. Soc., Seattle, WA, paper No. 228, 1990.

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4. H. Shih and F. Mansfeld, "Passivation in Rare Earth Metal Chlorides - A New Conversion Coating Process for Al Alloys," International Symposium on Corrosion Testing of Aluminum Alloys, ASTM, STP (in press), San Francisco, May 1990.

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6. H. Shih, Y. Wang, and F. Mansfeld, "Evaluation of the Surface Condition of Al Alloys by A Cyclic Polarization Method," submitted to Corr. Sci.

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12. B.A. Shaw, G.D. Davis, T.L. Fritz and K.A. Olver, J. Electrochem. Soc. 137, 359 (1990).

13. F. Mansfeld, "Concerning the Use of the Pitting Potential for Predictions of the Resistance of Al Alloys to Localized Corrosion," to be submitted to Corr. Sci.

14. F. Mansfeld, S. Lin, Y.C. Chen and H. Shih, J. Electrochem. Soc. 135, 906 (1988).

15. F. Mansfeld, "Optimization of Chromate Conversion Coatings on Al 7075-T73", Final Report, Contract No. 57-2928, Sandia National Laboratories, December 1989.

16. F. Mansfeld and H. Shih, "Chemical Passivation of Al Alloys and Al-Based Metal Matrix Composites in Rare Earth Metal Chlorides," Proc. 11th Int. Corrosion Cong., Florence, Italy, April 1990, paper No. 4.555.

17. H. Shih, Y. Wang and F. Mansfeld, "Evaluation of the Surface Condition of Al Alloys by a Cyclic Polarization Method," submitted to Corr. Sci.